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Finnish Chemistry Days and ChemBio Finland

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ABSTRACT BOOK

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Coordination team:

- Prof. Jan Lundell (Jyväskylä University)
- Prof. Antti Karttunen (Aalto University)
- Dr. Pekka M. Joensuu (Helsinki University)
- Prof. Markku Leskelä (Helsinki University)

Abstract book editors:

Jan Lundell, Antti Karttunen and Pekka Joensuu

Young Researcher Symposium,
Finnish Chemistry Days and ChemBio Finland,
Messukeskus, Helsinki, Finland 10.-11.4.2024

Scientific program: Thursday 11.4.2024

09:30 - 09:40 Welcome and opening (Pekka Joensuu, University of Helsinki)

Session: Building impact through chemistry (Chair: Jan Lundell, University of Jyväskylä)

09:40 – 10:00 KN: Janne Naapuri (University of Helsinki): Biocatalytic and chemoenzymatic synthesis of O-heterocycles from allenols

10:00-10:15 OC1 Rakesh Puttreddy (University of Jyväskylä): Halogen bonding modules for use in supramolecular materials

10:15-10:25 ST1 Daniel Langerreiter (Aalto University): A greener route to blue: Solid-state synthesis of phthalocyanines

10:25-10.35 ST2 Nguyen Le Phuoc (Eastern Finland University): A computational approach to carbene-metal-amide OLED materials

10:35 – 10:45 Break

Session: Electrifying chemistry (Chair: Jan Lundell, University of Jyväskylä)

10:45-11:00 OC2 Sara Lund (Åbo Akademi): From exfoliated graphite to graphene-based anodes for sustainable biophotovoltaic applications

11:00-11:15 ST3 Sara Hamed (Aalto University): Ni-rich positive electrode containing carbon nanotubes as conductive additive performance for high-power Li-ion batteries

11:15-11:25 ST4 Valtteri Oksanen (VTT Technical Research Center of Finland):Nickel-electrocatalyzed synthesis of bifuran-based monomers

11:25-11:35 ST5 Paulina Pršlja (Aalto University): CO_2 reduction over machine learned SnO_2/Carbon and CuNi nanocatalyst

11:35-11:45 ST6 Elavarasi Sundhararasu (University of Oulu): Fixed-bed column studies of heavy metal and ammonium removal by using alkali-activated adsorbent from industrial side streams

11:45 – 12:45 Lunch break

Session: **Enlightening chemistry** (Chair: Antti Karttunen, Aalto University)

12:45-13:00 **OC3** Sini Irvankoski (Aalto University) Blue-light induced 1,2-Chloro-N-Cl-amination of Olefins using N,N-Dichloro-tert-butylcarbamate reagents

13:00-13:10 **ST7** Yuliia Bardadym (University of Helsinki / Institute of Macromolecular Chemistry of NASU (UKR)): Structure and physical properties of epoxy composites cured under the influence of physical fields

13:10-13:20 **ST8** Adam Harmat (Aalto University): Computational approaches for the rational design of engineered silk-like proteins

13:20-13:30 **ST9** Erfan Kimiaei (Aalto University / North Carolina State University (USA)): Smart assembly of cellulose with biodegradable polyesters for barrier applications: From interfacial design to lifecycle assessment and end-life in aquatic environments

13:30-13:40 **ST10** Anna Lenardi (University of Helsinki): Chemically activated spruce organosolv lignin as carbocatalyst for heterogeneous oxidative dehydrogenations
(of N-heterocycles) in liquid phase

13:40-13:50 **ST11** Mikko Valkonen (Aalto University): The effect of a humidity gradient on tensioned micro-veneers

13:50 – 14:00 Break

Session: Making metals matter (Chair: Antti Karttunen, Aalto University)

14:00-14:15 **OC4** Jussi Lundahl (University of Helsinki) Germanium complexes in small molecule activation

14:15-14:25 **ST12** Navdeep Kajal (University of Jyväskylä):
Synthesis of novel metallogel and metal complexes using hexa-pyridine triphenylene ligands

14:25-14:35 **ST13** Anže Zupanc (University of Helsinki): Selective processing of coinage metals in sustainable ionic organic media

14:35-14:45 **ST14** Linfan Cui (Aalto University): Trash to treasure: Recovery of Pt with impurities in industrial process solutions

14:45-14:55 **ST15** Mikael Manninen (University of Oulu): Thermodynamics of aqueous vanadium solutions

14:55 – 15:45 Young Researcher poster session

Keynote talk:

KN	Janne Naapuri	HU	Biocatalytic and Chemoenzymatic Synthesis of O-Heterocycles from Allenols

Oral communications:

OC1	Rakesh Puttreddy	JYU	Halogen bonding modules for use in supramolecular materials
OC2	Sara Lund	ÅA	From Exfoliated Graphite to Graphene-Based Anodes for Sustainable Biophotovoltaic Applications
OC3	Sini Irvankoski	Aalto	Blue-light induced 1,2-Chloro-N-Cl-amination of Olefins using N,N-Dichloro-tert-butylcarbamate reagents
OC4	Jussi Lundahl	HU	Germanium complexes in small molecule activation

KN

Biocatalytic and Chemoenzymatic Synthesis of O-Heterocycles from Allenols

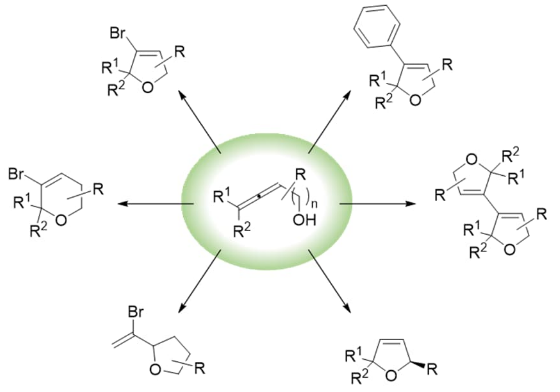
Janne M. Naapuri[1], and Jan Deska[1]

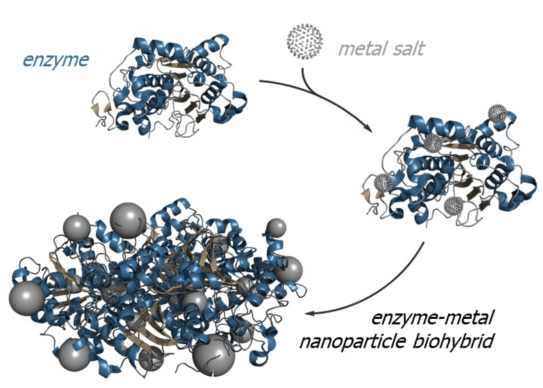
[1]University of Helsinki, A.I. Virtasen aukio 1, 00560 Helsinki, Finland

Nature’s enzymes hold great potential for the continued development of sustainable strategies in synthetic chemistry as highly efficient, selective and renewable biocatalysts, operating in mild reaction conditions. Here, the biocatalytic toolbox was expanded in the context of transforming allenic alcohols into a range of highly functionalized O-heterocycles.

In a non-conventional biphasic micellar reaction medium, both heme- and vanadate-dependent chloroperoxidases could catalyze brominative cyclizations of α-, β- and γ-allenols to furnish synthetically useful vinyl halide-containing furan and pyran derivatives. The non-hazardous biocatalytic design consumes simple bromide salts and hydrogen peroxide, though the latter can be replaced with D-glucose in a cascade process with glucose oxidase enzyme.[1]

The produced heterocycles were further valorized in chemoenzymatic one-pot processes in combination with well-established Pd cross-coupling techniques to reach arylated dihydrofurans step-efficiently.[2] Additionally, to combat common incompatibility-issues in chemoenzymatic designs, the metal- and biocatalysts could be combined as enzyme-metal nanoparticle biohybrids, which exhibit dual-activity as heterogeneous catalysts. Due to this bifunctionality, a nanobiohybrid could be used as catalyst for both transformations in the bromocyclization/cross-coupling method. The catalytic scope of the nanobiohybrids was taken further in a cascade process, where the combination of lipases with silver or gold would result in transformations of allenic acetates into enantiopure dihydrofurans via kinetic resolution hydrolysis and cycloisomerization.[3]





References

[1] Naapuri, J.M., Rolfes, J.D., Keil, J., Manzuna Sapu, C., Deska, J. *Green Chem.* 19 (2), (**2017**), 447-452; https://doi.org/10.1039/C6GC01926A
[2] Naapuri, J.M., Åberg, G. A., Palomo, J.M., Deska, J. *ChemCatChem* 13 (2), (**2021**), 763-769; https://doi.org/10.1002/cctc.202001619
[3] Naapuri, J.M., Losada-Garcia, N., Rothemann, R.A., Carmona Pichardo, M., Prechtl, M.H.G., Palomo, J.M., Deska, J. *ChemCatChem* 14 (16), (**2022**), e202200362; https://doi.org/10.1002/cctc.202200362

OC1

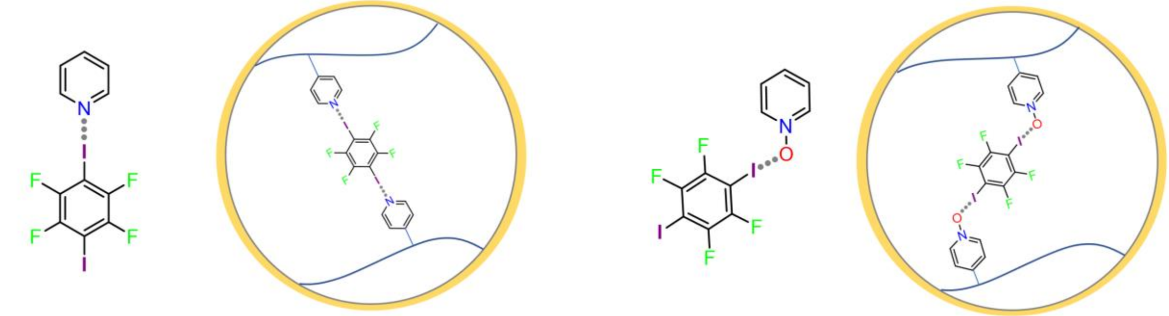
Halogen bonding modules for use in supramolecular materials

Rakesh Puttreddy[1]

[1]Department of Chemistry, University of Jyväskylä, Survontie 9 B, 40014 Jyväskylä, Finland

Email: rakesh.r.puttreddy@jyu.fi

Identifying robust non-covalent interaction modules is crucial for many applications including drug discovery and materials. Examples of such modules include hydrogen bonds, spanning from one to sextuple hydrogen-bonded motifs, which are frequently utilized for assembling simple molecular systems into more sophisticated and complex structures. The benefits of hydrogen bonding motifs include synthetic accessibility, directionality, and responsiveness to external stimuli. Similarly, halogen bonding, "a long-lost brother of hydrogen bonding", involving a polarized electron-deficient halogen atom interacting with an electron-rich counterpart, typically a nitrogen atom, has manifested itself in applications in a variety of fields. The halogen bonding to an oxygen atom, instead of a nitrogen atom, has attracted much less interest. The talk covers recent findings that demonstrate how a previous understanding of pyridine halogen bonding motifs has been used to generate new functional materials. It also summarizes aromatic N-oxide halogen bonding modules that can be useful to develop a range of supramolecular polymers.



Pyridine halogen bonding module

Supramolecular functional polymer

Pyridine N-oxide halogen bonding module

Supramolecular functional polymer?

Figure 1: Pyridine and pyridine N-oxide halogen bonding motifs and their use in supramolecular functional polymers

References

1. Puttreddy, R.; Rautiainen, J. M.; Yu, S.; Rissanen, K. *Angewandte Chemie* (2023), https://doi.org/10.1002/anie.202307372

2. Guo, H., Puttreddy, R., Salminen, T., Lends, A., Jaudzems, K., Zeng, H., & Priimagi, A. *Nature Communications*, *13*(1), (2022), 7436.

From Exfoliated Graphite to Graphene-Based Anodes for Sustainable Biophotovoltaic Applications

Sara Lund[1,2], Laura T. Wey[2], Tom Lindfors[1], Jan-Henrik Smått[1], Jouko Peltonen[1], Johan Bobacka[1], Rose-Marie Latonen[1] and Yagut Allahverdiyeva[2]

[1]Laboratory of Molecular Science and Engineering, Faculty of Science and Engineering, Åbo Akademi University, Henriksgatan 2, 20500 Turku (Åbo), Finland

[2]Photomicrobes group, Molecular Plant Biology, Department of Life Technologies, University of Turku, 20014 Turku, Finland

Due to the current climate crisis, there is an urgent demand to develop renewable energy technologies with materials that are abundant and preferably from renewable sources. In this work, graphene and graphene-nanocellulose composite films prepared by exfoliation of natural flake graphite are utilized as electrode materials in a biophotovoltaic device (BPVs) for green energy generation (Fig. 1). In a BPV device, photosynthetic microbes (e.g., cyanobacteria) convert solar energy into electricity using water as the source of electrons [1]. The electrode materials are spray-coated from few-layer graphene dispersions prepared by a green liquid-phase exfoliation method in an aqueous surfactant (sodium cholate) solution [2] or a suspension of cellulose nanocrystals (CNC) [3]. The developed shear exfoliation method is a fast and facile process which produces dispersions of high-quality few-layer graphene and graphene-CNC with a high concentration only after 2 h of exfoliation. Both CNC (extracted from cellulose) and sodium cholate are natural and non-toxic materials readily available from renewable sources. The prepared electrode films possess a high electrical conductivity and cyclic voltammetry experiments revealed that the films are electroactive and stable in aqueous electrolyte solutions. It was also found that the films are hydrophilic possessing roughness in nanoscale which are preferable qualities for anode materials in BPV devices. The average photocharge densities generated from illuminating the biofilms of cyanobacteria on the few-layer graphene and graphene-CNC films were 86.0 ± 32.0 μC cm^{-2} and 52.8 ± 23.2 μC cm^{-2}, respectively.

[1] Wey et al., ChemElectroChem, 6, 5375–5386 (2019)
[2] Lund et al., Carbon, 174, 123–131 (2021)
[3] Lund et al., Carbon Trends, 9, 100210 (2022)

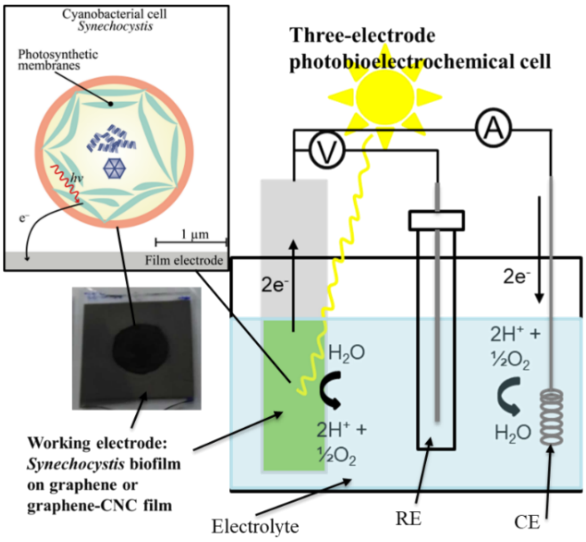


Fig. 1. Schematic representation of a cyanobacterial cell and a three-electrode biophotovoltaic system with a photograph of graphene-CNC working electrode coated with a biofilm of cyanobacterial cells

Blue-light induced 1,2-Chloro-*N*-Cl-amination of Olefins using *N*,*N*-Dichloro-*tert*-butylcarbamate reagents

Sini S. Irvankoski[1], Michael Davenport[2], Daniel Ess[*,2], and Juha H. Siitonen[*,1]

[1]Department of Chemistry and Material Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.
[2]Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States.

Direct amination of olefins has gathered a lot of attention in the recent years, as nearly all modern materials and pharmaceuticals contain nitrogen. Different carbamate-based aminations have found scant uses over the years but harnessing them for more widespread use in synthetic chemistry is yet to be established. In particular, *N*-chlorocarbamates have been previously applied in aminochlorinations, chlorinations, and a range of other transformations using catalytic metals (Cr, Cu), thermal activation or UV irradiation with sensitive and expensive photocatalysts.[1,2] Their broader utility in synthetic chemistry is largely limited by the lack of functional group tolerance and complications related to the required activation methods. While the homolytic cleavage of N–Cl bonds using UV light has been widely studied and even utilized in water purification, activation of N–Cl bonds using visible blue light is currently unknown.

Herein we introduce such a blue light induced aminochlorination of unactivated olefins. The method is a new functionalization tool allowing the direct installation of nitrogen atoms to olefinic molecules in a streamlined fashion. By using blue light as a mild activator, our work demonstrates that a simple reagent *N*,*N*-dichloro-*tert*-butylcarbamate can circumvent numerous of the prior issues, and a wide range of functionally diverse olefins are successfully aminochlorinated. The mechanistic studies of this transformation suggest that dichlorocarbmates undergo a photochemical excitation to yield a nitrogen and a chlorine radical which then react with the olefinic double bond. With this method aminochlorination is achieved energy effectively from readily available starting materials without harsh reaction conditions nor highly specialized chemical equipment.

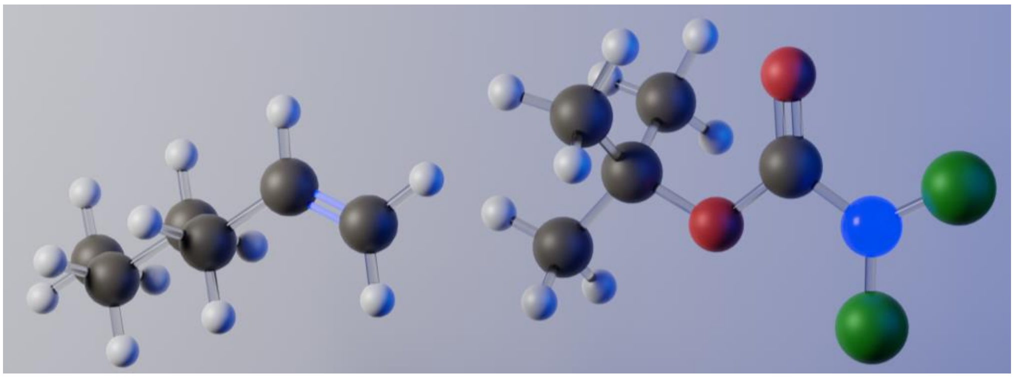


Figure 1: New blue light induced method allows direct installation of nitrogen to olefinic compounds (1-hexene, left) in a streamlined fashion using readily available starting materials (*N*,*N*-Dichloro-*tert*-butylcarbamate, right).

References

[1] Lu, X.; Xiao, B.; Zhang, Z.; Gong, T.; Su, W.; Yi, J.; Fu, Y.; Liu, L. *Nat. Commun.* 7 (1), (**2016**), 1–8; https://doi.org/10.1038/ncomms11129.

[2] Rivas, M.; Palchykov, V.; Jia, X.; Gevorgyan, V. *Nat Rev Chem*,, 6 (8), (**2022**), 544–561; https://doi.org/10.1038/s41570-022-00403-8.

OC4

Germanium complexes in small molecule activation

Jussi Lundahl[a], and Petra Vasko[a]

[a] University of Helsinki, Department of Chemistry, A.I. Virtasen Aukio 1, 00560 Helsinki, Finland

The transformation of greenhouse gases (e.g., CO_2, N_2O, CH_4) into value-added chemicals is a valuable target. Currently, the focus of the research is on small molecule activation using various transition metal complexes [1]. There is also a growing interest in using group 13 and 14 compounds to avoid potentially toxic noble metals. It has been recently demonstrated that main-group compounds can mimic the reactivity of transition metals.[2–6] These reactions are typically stoichiometric, and catalytic turnover efficiency is far from what is needed in large-scale applications. However, low-valent main group compounds can exhibit a very rich and broad reactivity as they can activate a wide variety of X-H bonds (X = H, C, Si, O, N).[7]

In an effort to see what trends are emerging particularly in CO_2 activation using germanium, we are now building a library of compounds based on amino-silyl substituents (Figure 1a). Additional stabilization can be achieved by the coordination of cyclic alkyl amino carbenes (CAACs) to germanium. In preliminary reactivity studies, 1b reacts irreversibly with CO_2 (Figure 1b). In this contribution, we will discuss the structural features of these compounds and how they relate to their reactivity with small molecules.

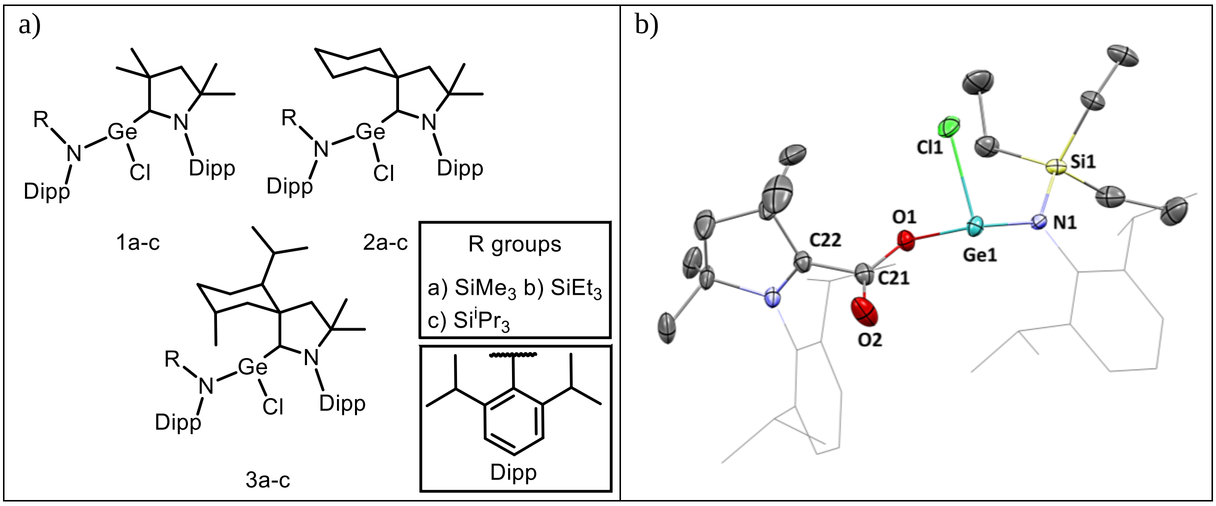


Figure 1: a) Targeted molecule library. b) A molecular structure of 1b with CO_2.

References

[1] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*, **1966**, *I* (0), https://doi.org/10.1039/J19660001711.

[2] Lazar, M. D.; Mihet, M.; Dan, M. *Comprehensive Renewable Energy*; Elsevier, 2022; https://doi.org/10.1016/b978-0-12-819727-1.00032-7.

[3] Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. *Science*, **2009**, *325* (5948). https://doi.org/10.1126/science.1176443.

[4] Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science*, **2006**, *314* (5802). https://doi.org/10.1126/science.1134230.

[5] Power, P. P. *Nature*, **2010**, *463* (7278). https://doi.org/10.1038/nature08634.

[6] Weetman, C.; Inoue, S. *ChemCatChem*, **2018**, *10* (19). https://doi.org/10.1002/cctc.201800963.

[7] Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; *Chem Rev*, **2018**, *118* (19). https://doi.org/10.1021/acs.chemrev.8b00079.

Short talks:

ST1	Daniel Langerreiter	Aalto	A greener route to blue: Solid-state synthesis of phthalocyanines
ST2	Nguyen Le Phuoc	Joensuu (UEF)	A computational approach to carbene-metal-amide OLED materials
ST3	Sara Hamed	Aalto	Ni-rich Positive Electrode Containing Carbon Nanotubes as Conductive Additive Performance for High-power Li-ion Batteries
ST4	Valtteri Oksanen	VTT	Nickel-Electrocatalyzed Synthesis of Bifuran-Based Monomers
ST5	Paulina Pršlja	Aalto	CO_2 reduction over Machine Learned SnO_2/Carbon and CuNi nanocatalyst
ST6	Elavarasi Sundhararasu	Oulu (UO)	Fixed-bed column studies of heavy metal and ammonium removal by using alkali-activated adsorbent from industrial side streams
ST7	Yuliia Bardadym	HU/NASU (UKR)	Structure and Physical Properties of Epoxy Composites Cured Under the Influence of Physical Fields
ST8	Adam Harmat	Aalto	Computational approaches for the rational design of engineered silk-like proteins
ST9	Erfan Kimiaei	Aalto/NCSU (USA)	Smart Assembly of Cellulose with Biodegradable Polyesters for Barrier Applications: From Interfacial Design to Lifecycle Assessment and End-life in Aquatic Environments
ST10	Anna Lenarda	HU	Chemically activated Spruce Organosolv Lignin as Carbocatalyst for Heterogeneous Oxidative Dehydrogenations (of N-heterocycles) in Liquid Phase
ST11	Mikko Valkonen	Aalto	The Effect of a Humidity Gradient on Tensioned Micro-Veneers
ST12	Navdeep Kajal	JYU	Synthesis of novel metallogel and metal complexes using hexa-pyridine triphenylene ligands
ST13	Anže Zupanc	HU	Selective Processing of Coinage Metals in Sustainable Ionic Organic Media

ST14	Linfan Cui	Aalto	Trash to Treasure: Recovery of Pt with Impurities in Industrial Process Solutions
ST15	Mikael Manninen	Oulu	Thermodynamics of Aqueous Vanadium Solutions

A greener route to blue: Solid-state synthesis of phthalocyanines

Daniel Langerreiter[a], Mauri Kostiainen[a], Sandra Kaabel[a], Eduardo Anaya Plaza[a]

[a] Department of Bioproducts and Biosystems

Aalto University 02150 Espoo (Finland)

Sustainability and environmentally friendly alternatives of producing and synthesizing chemicals are gaining more importance and are heavily investigated, aligned with the UN sustainable development goals #6 and #12 – clean water and sanitation, and responsible consumption and production, respectively. A greener route to achieve these goals relies on solid-state reactions, where solvents are drastically reduced.[1] Especially mechanochemistry[2,3] has gained importance, not just in organic synthesis but also in polymer science or material chemistry. [4–6]

One field which might benefit from a greener synthesis pathway is the synthesis of organic dyes, where water-miscible, high-boiling point solvents are still widely used. Mechanochemical and solid-state synthesis of dyes provide an opportunity for avoiding the use of a large amount of solvent, which could be a threat to water quality and the environment, while bringing economic benefits to industry.

Within the organic dyes, phthalocyanines (Pcs) are one of the most famous onea[7], with a broad applicability in optoelectronics, catalysis, sensing and nanomedicine.[8,9] At the current state, phthalocyanines are synthetized in high boiling organic solvents, like dimethylaminoethanol (DMAE), which is a flammable, corrosive, and bioactive substance, miscible with water and harmful to the environment.

Here we show a new solid-state approach for the synthesis of phthalocyanines, in which we reduce up to 100- fold the amount of the solvent. Through systematic screening of various reaction parameters, carried out by ball-milling and aging, we show the influence the different variables like temperature, presence of a template, and the amount and role of DMAE in the conversion of *t*Bu phthalonitrile to tetra-*t*Bu phthalocyanine.

Reference:

[1] K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025–1074.

[2] V. Štrukil, M. D. Igrc, L. Fábián, M. Eckert-Maksić, S. L. Childs, D. G. Reid, M. J. Duer, I. Halasz, C. Mottillo, T. Friščić, *Green Chem.* **2012**, *14*, 2462.

[3] S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413–447.

[4] S. Tanaka, in *Met. Fram. Biomed. Appl.*, Elsevier, **2020**, pp. 197–222.

[5] A. Krusenbaum, S. Grätz, G. T. Tigineh, L. Borchardt, J. G. Kim, *Chem. Soc. Rev.* **2022**, *51*, 2873–2905.

[6] X. Li, M. Baldini, T. Wang, B. Chen, E. Xu, B. Vermilyea, V. H. Crespi, R. Hoffmann, J. J. Molaison, C. A. Tulk, M. Guthrie, S. Sinogeikin, J. V. Badding, *J. Am. Chem. Soc.* **2017**, *139*, 16343–16349.

[7] M. O. Senge, N. N. Sergeeva, K. J. Hale, *Chem. Soc. Rev.* **2021**, *50*, 4730–4789.

[8] M. Urbani, G. de la Torre, M. K. Nazeeruddin, T. Torres, *Chem. Soc. Rev.* **2019**, *48*, 2738–2766.

[9] M. Wang, K. Torbensen, D. Salvatore, S. Ren, D. Joulié, F. Dumoulin, D. Mendoza, B. Lassalle-Kaiser, U. Işci, C. P. Berlinguette, M. Robert, *Nat. Commun.* **2019**, *10*, 3602.

A computational approach to carbene-metal-amide OLED materials

Nguyen Le Phuoc[1], Alexander Romanov[2], and Mikko Linnolahti[1]

[1]Department of Chemistry, University of Eastern Finland, FI-80101 Joensuu, Finland

[2]Department of Chemistry, University of Manchester, Oxford Rd., Manchester M13 9PL, UK

Two-coordinate coinage metal complexes are promising materials suitable for utilization in organic light-emitting diode (OLED) devices. This assertion is attributed to their capacity to achieve photoluminescence (PL) quantum yields (PLQY) at unity, arising from either phosphorescence or thermally activated delayed fluorescence (TADF). [1], [2], [3]

Aiming to systematically investigate their PL properties, we conducted a density functional theory study encompassing over 60 gold-centered carbene–metal–amides (CMAs) with a diverse array of cyclic (alkyl)(amino)carbenes (CAACs). Computational findings reveal that these CMAs exhibit efficient TADF behavior when a compromise is attained between oscillator strength coefficient and exchange energy between the lowest excited singlet (S_1) and triplet (T_1) states. These parameters are strongly correlated with vertical S_0-S_1 and S_0-T_1 excitation energies as well as HOMO-LUMO overlap integral, where the HOMO is primarily localized on the amide and the LUMO along the metal–carbene bond. The complexes adopt a nearly coplanar geometry of carbene and amide ligands in the S_0 and T_1 states, whereas they undergo a rotation to a perpendicular orientation in the S_1 state. This geometric transformation is accompanied by a reduction in the S_1-S_0 oscillator strength, which diminishes from its maximal value at coplanar geometry to an approximate null value at rotated geometry. [4]

Guided by calculated results, a novel CMA complex, denoted as (^{Et2}CAAC)Au(carbazolide), is synthesized with excellent stability and remarkable PL properties, including PLQY approaching unity and an excited state lifetime of 10^6 s^{-1}. [4] Furthermore, the computational outcomes are instrumental in elucidating the PL characteristics, i.e., ^{3}MLCT-character phosphorescence and variations in PLQY values, observed in fast and bright phosphorescent diamidocarbene–metal(I)–carboranyl copper and gold complexes, which show up to 68% PLQY and microsecond lifetimes. [5]

References

[1] Di, D., Romanov, A.S., Yang, L., Richter, J.M., Rivett, J.P., Jones, S., Thomas, T.H., Jalebi, M.A., Friend, R.H., Linnolahti, M., Bochmann, M., Credgington, D. *Science*. 356 (6334), (**2017**), 159; https://doi.org/10.1126/science.aah4345
[2] Yersin, H., Czerwieniec, R., Shafikov, M. Z., Suleymanova, A. F. *ChemPhysChem*. 18 (24), (**2017**), 3508; https://doi.org/10.1002/cphc.201700872
[3] Hossain, J., Akhtar, R., Khan, S. *Polyhedron*. 201 (29), (**2021**), 115151; https://doi.org/10.1016/j.poly.2021.115151
[4] Phuoc, N.L., Brannan, A.C., Romanov, A.S., Linnolahti, M. *Molecules*. 28 (11), (**2023**), 4398; https://doi.org/10.3390/molecules28114398
[5] Powley, S.L., Riley, C., Cho, H., Phuoc, N.L., Linnolahti, M., Greenham, N., Romanov, A.S. *Chem. Commun*. 59 (80), (**2023**), 12035; https://doi.org/10.1039/D3CC04091G

Ni-rich Positive Electrode Containing Carbon Nanotubes as Conductive Additive Performance for High-power Li-ion Batteries

Sara Hamed, Tanja Kallio
Department of Chemistry and Materials Science (CMAT), School of Chemical Engineering,
Aalto University, 02150, Espoo, Finland
Sara.hamed@aalto.fi

Li-ion batteries (LIBs) nowadays have been used widely for applications such as the electric vehicles, portable electronic devices, and stationary energy storage industries because of their high energy and power density and reliable lifetime [1]. However, the current energy density and power density of LIBs less meet the performance required by portable electric devices and EVs. To meet these requirements, carbon black is a commonly used conductive agent to reduce the internal resistance of the electrode and provide electronic pathways in the electrodes through “point-to-point” contact between acetylene black and active material particles; however, it is disadvantageous because of 0D material characteristics. On the other hand, carbon nanotubes (CNTs) are promising material as a conductive agent for reducing the electrode's internal resistance due to their high aspect ratio and forming three-dimensional (3D) conductive networks by the “line-to-line” contact with other CNTs and “line-to-point” contact with active material particles [2]. Since CNT and CB are inclined to agglomerate, only CNTs or sole CBs might not be capable of efficiently building a conductive network in the electrode. It is necessary to avoid self-aggregation while constructing a three-dimensional carbon network by sufficiently utilizing the advantages of one-dimensional (1D) CNT and zero-dimensional (0D) CB.

In this study, the properties of a Li-Ni0.6Co0.2Mn0.2O2 positive electrode were investigated by varying the electrode composition. The specific capacity, coulombic efficiency, and rate capability of the electrode were significantly affected by the ratio of carbon nanotubes (CNTs) to carbon black (CB) and the total amount of the additives. The rate capability of the electrode is enhanced by increasing the amount of CNTs up to 30 wt-% in the total conductive carbon share, when the PVDF and active material amounts were fixed to 1 % and 98 %, respectively. The result is explained by the CNT additive's electronic conducting effect, which resulted in higher discharge specific capacity. The results of a long-term cycling experiment indicate that the mechanical integrity of the electrode's composition plays a crucial role in its durability. Moreover, the operando XRD and dilatometry experiments demonstrate other benefits brought by CNTs for the NMC622 positive electrodes. The presence of CNTs in the electrode reduces the irreversible height change that occurs during cycling and minimizes anisotropic lattice changes compared to the reference electrode and thus improve the capacity retention during long term cycling.

References

[1] Hou, W., Zhu, D., Ma, S., Yang, W., Yan, H., & Dai, Y. High-voltage nickel-rich layered cathodes in lithium metal batteries enabled by a sulfolane/fluorinated ether/fluoroethylene carbonate-based electrolyte design. *Journal of Power Sources, 517* (2022), 230683.

[2] Cheon, S. E., Kwon, C. W., Kim, D. B., Hong, S. J., Kim, H. T., & Kim, S. W. Effect of binary conductive agents in LiCoO2 cathode on performances of lithium ion polymer battery. *Electrochimica acta, 46*(4) (2000), 599-605

ST4

Nickel-Electrocatalyzed Synthesis of Bifuran-Based Monomers

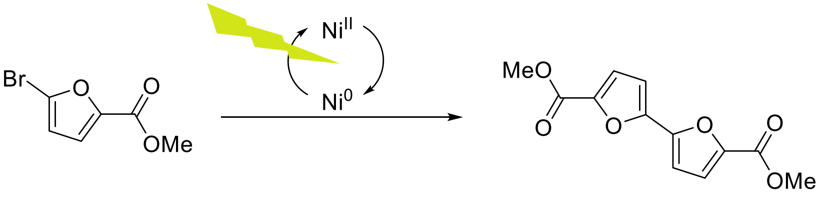
Valtteri Oksanen[1], Sari Rautiainen[1], and Tom Wirtanen[1]

[1]Chemical & Polymer Synthesis, VTT Technical Research Centre of Finland, 02044 Espoo, Finland

More sustainable alternatives are needed for high-volume chemicals such as polymers due to climate change and increasing greenhouse gas emissions. One of the most potential new materials are furan-based polymers, such as polyethylene furan-2,5-dicarboxylate (PEF), which has been envisioned as a replacement for polyethylene terephthalate (PET) and is obtained from lignocellulosic biomass. Considerably less research has been devoted to the synthesis and polymerization of bifurans. These derivatives are readily obtained from hemicellulose, the second most abundant polysaccharide, and they display interesting complementary material properties, as a sole monomer or co-monomer in PEF, such as increased UV resistance, glass transition temperature and O_2 barrier properties compared to PEF.[1]

The synthesis of bifurans is unfortunately far less established than PEF monomers. One of the most viable routes is the homocoupling of bromo furan carboxylates, but the literature methods have some major drawbacks, such as expensive palladium catalysts, and poisonous CO or metal powders as reductants.[2, 3] In this respect, nickel-electrocatalyzed reductive homocoupling of aryl bromides would be an interesting alternative as it would allow to use more inexpensive catalyst and circumvent the need for stoichiometric reductants with electrons. However, the current literature examples employ a sacrificial anode which makes this method as problematic as using stoichiometric metal powders as reductants. Moreover, the nickel-electrocatalyzed synthesis of bifurans has not been described previously in the literature.

We have recently developed reaction conditions for reductive nickel-electrocatalysis particularly suitable for the synthesis bifuran-based monomers.[3] The method circumvents the use of sacrificial anode by utilizing triethanolamine oxidation as the anodic counter reaction and is performed in an undivided cell with graphite electrodes. The method can be extended to bithiophene and biaryl monomers as well, and in all cases, the product separation is achieved effortlessly by precipitation with water. Scale-up studies indicate that the developed method could be used for larger scale synthesis of 2,2-bifuran-5,5-dicarboxylic acid monomer, paving the way for sustainable synthesis of these key monomers.



References

[1] a) Kainulainen, T.P. Hukka, T.I. Özeren, H.D. Sirviö, J.A. Hedenqvist, M.S. Heiskanen, J.P. *Biomacromolecules*, 21 (2), (**2020**), 743–752; https://doi.org/10.1021/acs.biomac.9b01447 b) Kainulainen, T.P. Parviainen, T.A.O. Sirviö, J.A. McGeachie, L.J.R. Heiskanen, J.P. *ACS Macro Lett.* 12 (2), (**2023**), 147–151; https://doi.org/10.1021/acsmacrolett.2c00743
[2] a) Lee, K. Lee, P.H. *Tetrahedron Lett.* 49 (27), (**2008**), 4302–4305; https://doi.org/10.1016/j.tetlet.2008.04.123 b) Zhu, J. Lei, Y. Chen, Z. Liao, Y. Yin, G. *Mol. Catal*. 513 (**2021**), 111814, https://doi.org/10.1016/j.mcat.2021.111814
[3] Oksanen, V. Rautiainen, S. Wirtanen, T. *Chem. Eur. J.* (**2023**), e202302572, https://doi.org/10.1002/chem.202302572

ST5

CO_2 reduction over Machine Learned SnO_2/Carbon and CuNi nanocatalyst

Paulina Pršlja[1], Junjie Shi [1], Tanja Kallio[1] and Miguel Caro[1]

[1] Department of Chemistry and Material Science, Aalto University, Espoo, Finland

The development of efficient and selective electrochemical CO_2 reduction catalysts remains a challenge. Copper-based materials are the only catalysts that generate C_2 products [1], whereas post-transition metals are selective toward $HCOO^-$ production [2-3]. Tuning the structural features and elemental composition can facilitate the selective production of a single product. However, the search for realistic selective atomic sites increases the challenge of current computational methods and calls for the development of new techniques for efficient screening.

Herein SnO_2 and CuNi nanoparticles were generated via Machine Learning interatomic potential, particularly Gaussian Approximation Potential (GAP) [4-7], to assess to investigate the thermodynamic stability of various size effects and composition ratios under high-temperature annealing, respectively. Selectivity was tested using selectivity descriptors on the identified active sites at different coverage levels.

[1] H. Xiea, T. Wanga, J. Lianga, Q. Lia, S. *Sun, Nano Today* **2018**, 21, 41-54.
[2] S. Zhao, S. Li, T. Guo, S. Zhang, J. Wang, Y. Wu, Y. Chen, *Nano-Micro Lett*. **2019**, 11-62
[3] M. F. Philips, D. Pavesi, T. Wissink, M. C. Figueiredo, G-J. M. Gruter, Marc T. M. Koper, and K. J. P. Schouten, *ACS Appl. Energy Mater*. **2022**, 5, 2, 1720–1730
[4] V.L. Deringer, M.A. Caro, and G. Csányi, *Adv. Mater*. **2019**, 31, 1902765.
[5] A.P. Bartók, M.C. Payne, R. Kondor, and G. Csányi, *Phys. Rev. Lett*. **2010**, 104, 136403. [6] A.P. Bartók, R. Kondor, and G. Csányi, *Phys. Rev. B* **2013**, 87, 184115.
[7] M.A. Caro, *Phys. Rev. B* **2019**, 100, 024112.

Fixed-bed column studies of heavy metal and ammonium removal by using alkali-activated adsorbent from industrial side streams

Elavarasi Sundhararasu, Hanna Runtti, Sari Tuomikoski, Teija Kangas, Ulla Lassi

University of Oulu, Research Unit of Sustainable Chemistry, P.O. Box 4300, FI-90014 Oulu, Finland

Water pollution by heavy metal contaminants is a global concern, emphasizing the urgent need for cost-effective, and eco-friendly wastewater purification solutions [1]. Using mineral industrial side streams for this purpose could promote a circular economy. With the increasing demand for efficient water treatment technologies worldwide, cost-effective alkali-activated adsorbents based on mineral industrial side streams may be employed [1,2]. This research focuses on the stability of alkali-activated materials as efficient adsorbents for nickel and ammonium removal. Industrial side streams (blast furnace slag, Linz-Donawitz slag, ladle slag, analcime) are used as raw materials. Characterization includes X-ray diffraction, X-ray fluorescence, surface area measurements, Fourier-Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy, and leaching tests.

Nickel adsorption/desorption experiments were performed in fixed bed column using 0.5 cm bed height. Flow rate (5 mL/min) and concentration (50 mg/L) were evaluated for the removal of nickel ions [1]. In the case of ammonium removal, flow rates were 5, 10 and 20 mL/min and initial concentration was 40 mg/L [2]. Alkali-activated adsorbents were regenerated in several cycles by using sodium-based regeneration agents. Experimental values were fitted with Thomas, Bohart–Adams and Yoon–Nelson breakthrough curve models and the models fitted well with the experimental data with a high R^2 value.

Batch adsorption experiments were conducted to ammonium to explore the impact of initial concentration (from 5 to 1000 g/L), adsorbent dosage (from 1 to 20 g/L) and contact time (from 1 minute to 24 hours). Ammonium adsorption onto alkali-activated analcime surfaces was analyzed through various isotherm models, including Langmuir, Freundlich, Sips, and Bi-Langmuir. Moreover, the experimental data were evaluated using pseudo-first-order, pseudo-second-order, and Elovich models [3]. The findings indicate that the alkali-activated materials are promising materials for efficiently removal of nickel and ammonium from water sources.

References

1. Sundhararasu, E.; Tuomikoski, S.; Runtti, H.; Hu, T.; Varila, T.; Kangas, T.; Lassi, U. Alkali-Activated Adsorbents from Slags: Column Adsorption and Regeneration Study for Nickel(II) Removal. *ChemEngineering* **2021**, *5*, 13, doi:10.3390/chemengineering5010013.
2. Sundhararasu, E.; Runtti, H.; Kangas, T.; Pesonen, J.; Lassi, U.; Tuomikoski, S. Column Adsorption Studies for the Removal of Ammonium Using Na-Zeolite-Based Geopolymers. *Resources* **2022**, *11*, 2–13, doi:10.3390/resources11120119.
3. Runtti, H.; Sundhararasu, E.; Pesonen, J.; Tuomikoski, S.; Hu, T.; Lassi, U.; Kangas, T. Removal of Ammonium Ions from Aqueous Solutions Using Alkali-Activated Analcime as Sorbent. *ChemEngineering* **2023**, *7*, 5, doi:10.3390/chemengineering7010005.

Structure and Physical Properties of Epoxy Composites Cured Under the Influence of Physical Fields

Yu. Bardadym
University of Helsinki, Finland
Institute of Macromolecular Chemistry of NASU, Ukraine

Epoxy polymer (EP) is an excellent base for composite materials due to its superb adhesion, high strength, low cure shrinkage, lack of melting, high chemical and thermal stability, excellent mechanical and electrical properties. In the manufacture of functional composite epoxy materials, the control of agglomeration and orientation of the filler in the polymer matrix is extremely important. To date, there are several approaches to obtain polymer composites with oriented fillers. Among these approaches, the physical fields (PF) are very attractive due to the ease of manipulating the alignment of the filler in desired directions, even when the filler may not have sufficient magnetic properties.

Samples of composites were formed from ER with was 3 vol. % CdO, PbO or Cr_2O_3. The influence of constant magnetic (CMF) or electric (CEF) fields were $2 \cdot 10^5$ A/m and $1.5 \cdot 10^4$ V/m. All curing processes were done at 20 – 25 °C for 24 hours. In the scattering region $2\theta = 26.11^o$ and $2\theta = 29^o$ in the structure of the crystalline phase CdO the disappearance of part of the reflexes was observed, and for others the change in intensity after the influence of PF. However, reflexes $2\theta = 30.2^o$; 33.0^o; 38.3^o and 55.24^o with the highest intensity remained unchanged, which indicated the stability of the CdO crystal system in the composition of composites. Samples with PbO were characterized by the presence of 17 main reflexes in the range $2\theta = 28 – 58^o$. New reflexes in areas $2\theta = 26^o$, 50.6^o, 54.6^o appeared after the influence of PF. This indicates a redistribution of intensities and a partial angular shift of the maxima of certain reflexes. Significant changes in the angular position and intensity of the main maxima of hexagonal syngony were not observed for samples with Cr_2O_3. However, the intensity for the reflexes d014, d111 and d110 varied depending on the curing conditions of the composites. The average crystallite size for these samples were 6 – 18 nm.

It should be noted changes in the topological structure were observed for unfilled EP. This was due to the influence of external CPF on the polycondensation reaction and the formation of a three-dimensional chemical network. Differences in the influence of CPF were manifested after reaching the range of 88 - 94 °C (relaxation of segments of intermolecular fragments of EP). Changes in the temperature range 97 - 167 K indicate that the use of CMF or CEF to form the structure of the EP allows you to change the packing density of the chemical network relative to its initial state (without PF).

Differences of the influence of PF on the dielectric characteristics occur after reaching the region 88 - 94 °C. The high-temperature transition in the region 134 - 136 °C can be related to the relaxation in the biphenylolpropane fragment, which is stored regardless of the external conditions of influence. The orientation effect of PF increases the free volume of the molecular chains of a chemical grid, which results in a decrease of glass transition temperature by 8 °C and 14 °C for CMF and CEF, respectively.

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Computational approaches for the rational design of engineered silk-like proteins

Adam L. Harmat[1,2,*], Dmitry Tolmachev[1,2], Alberto Scacchi[2,3], and Maria Sammalkorpi[1,2,3]
[1]Department of Chemistry and Materials Science, Aalto University, Espoo, Finland
[2]Academy of Finland Center of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, Espoo, Finland
[3]Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland
*adam.harmat@aalto.fi, Soft Materials Modelling group, Aalto University

Condensate formation, i.e. liquid-liquid phase separation (LLPS) of protein solutions in living cells is an established pre-assembly step associated with basic biological cell function and several pathological conditions. These include, e.g., Alzheimer's disease, amyotrophic lateral sclerosis, and Parkinson's disease [1]. LLPS is also an intermediate step in the formation of advanced biobased materials, such as amyloids, mussel feet adhesives, squid beaks or silk-like fibers. Protein structural materials exhibit exceptional mechanical properties whilst being biodegradable and lightweight. The rational design of protein condensates is necessary for understanding LLPS and paving the way for engineered biosynthetic protein materials.

To this purpose, we investigate engineered silk-like proteins using computational modelling to explore molecular level interactions and their implications on LLPS as observed in experiments [2,3]. Silk-like proteins have two folded domains connected by an intrinsically disordered region (IDR), making them an ideal model system for systematically investigating the interplay of folded and disordered regions in protein assembly.

Here, we present a methodology advancement based on using protein-protein docking combined with molecular dynamics simulations to study interactions between the folded domains. We demonstrate the approach for a well-characterized ubiquitin system after which we map the response of four different folded domains matching our experimentally realized systems [4,5]. The simulations results show a difference in the type and anisotropicity of the interactions that regulate coacervate propensity and the physical properties of the coacervates. A mesoscale coarse-grained model was constructed to better understand the protein assembly process. The results highlight a complex interplay of folded and IDR domain interactions.

References

[1] Albertti, S. *Curr. Biol.* 27 (20), (**2017**), R1091-R1102.
[2] Batys, P, Fedorov, D., Mohammadi, P., Lemetti, L., Linder, M.B., Sammalkorpi M., *Biomacromolecules* 22 (2), **(2021)**, 690-700.
[3] Lemetti, L., Scacchi, A., Yin, Y., Shen, M., Linder, M.B., Sammalkorpi, M., and Aranko, A.S., *Biomacromolecules* 23 (8), **(2022)**, 3142–3153.
[4] Fedorov, D., Escalona, N.R., Tolmachev, D., Harmat, A.L., Scacchi, A., Sammalkorpi, M., Aranko, A.S., and Linder, M.B., *submitted* **(2023)**.
[5] Harmat, A.L., Tolmachev, D., and Sammalkorpi, M., *under preparation* (**2023**).

Smart Assembly of Cellulose with Biodegradable Polyesters for Barrier Applications: From Interfacial Design to Lifecycle Assessment and End-life in Aquatic Environments

Erfan Kimiaei[1,2], Nathalie Lavoine[2], Richard Venditti[2], Monika Österberg[1]*
[1]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo, Finland
[2]Department of Forest Biomaterials, College of Natural Resources, North Carolina State University, Raleigh, United States

Natural and biodegradable polymers like cellulose have shown great potential to replace fossil-based plastics. However, its susceptibility to water and moisture poses challenges when blending with hydrophobic polymers, thereby limiting its widespread use. To address these problems, we innovatively introduced the Pickering emulsion as a versatile template for combining hydrophilic nanocellulose with hydrophobic polyesters such as polycaprolactone (PCL) with the help of lignin nanoparticles (LNPs) as an interfacial compatibilizer. Combining LNPs with nanocellulose enabled the production of an ultra-stable PCL emulsion. After drying the emulsion, free-standing composite films with an even dispersion of PCL onto the surface of the nanocellulose network were achieved. The composites exhibited unprecedented mechanical properties in both dry and wet states (tensile strength up to 200MPa and 87MPa, respectively) due to the favorable intercomponent interactions. This interfacial design conferred additional properties to nanocellulose such as great protection against water vapor, UV, and oxidation, making it outstanding for the packaging application. Furthermore, the composite films exhibited excellent biodegradability between 85% and 97% after 42 days of exposure to natural seawater and simulated freshwater. Thus, this interfacial strategy offers a facile route to design multifunctional cellulose-based composites using only lignocellulosic and biodegradable polymers without any chemical modifications that harness the natural biodegradability and maximum benefit of each constituent. In the end, from a sustainability perspective, the life cycle assessment (LCA) of such biocomposite was conducted to evaluate the environmental impacts associated with biocomposite production in comparison with productions of low-density polyethylene (LDPE), a common fossil-based material in the packaging industry. Furthermore, a production hotspot was identified to determine in which scenarios the biocomposite could be a more environmentally friendly alternative than LDPE films within their well-established technology. This information is crucial to help the industry fill the gap in replacing traditional plastics by biobased products with a sustainable approach.

ST10

Chemically activated Spruce Organosolv Lignin as Carbocatalyst for Heterogeneous Oxidative Dehydrogenations (of N-heterocycles) in Liquid Phase

Anna Lenarda,[a] Michele Melchionna,[b] Paolo Fornasiero, [b] Michael Hummel,[c] and Juho Helaja*[a]

[a]Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O. Box 55, 00014 Helsinki, Finland;
[b]Department of Chemical and Pharmaceutical Sciences, INSTM, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy
[c]Department of Bioproducts and Biosystems, Aalto University, Vuorimiehentie 1, 02150 Espoo, Finland

Activated carbons obtained from organosolv lignin by chemical activation with KOH and oxidized with diluted HNO_3 were studied as catalysts for aerobic oxidative dehydrogenation (ODH) reactions. The structure/activity relationship was investigated through multiple techniques revealing the crucial role of specific pore size and oxygen functionalities distribution in promoting two mechanistically archetypical ODH probe reactions: 1) the tetrahydroquinoline (THQ) aromatization, which represents ODH triggered by hydride transfer and 2) the 2-phenyl indole homocoupling reaction, a model for single electron transfer (SET) promoted reactions. In particular, the catalytic activity, correlating with oxygen functionalities distribution on the basis of X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) analysis, was associated with the C=O surface functionalities, as confirmed by blocking experiments with 2,2,2-trifluoroethyl hydrazine. Kinetic profiling tools were employed to assess THQ ODH product inhibition effects on the overall yield of the process as well as the extent of stoichiometric activity of the carbocatalyst. The breadth of the developed catalysts' applicability was explored through selected relevant ODH reactions.

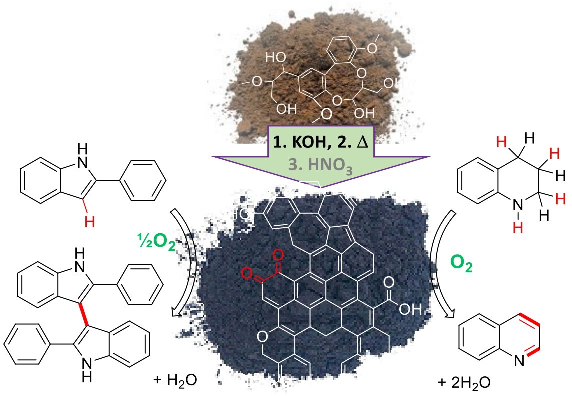

Figure 1: Graphical representation of the catalytic system proposed for the two model reactions explored in this work

References
[1] Lenarda, A.; Melchionna, M.; Aikonen, S.; Montini, T.; Fornasiero, P.; Hu, T.; Hummel, M.; Helaja J.; *ACS Catal.* 13 (17), (**2023**), 11362; https://doi.org/10.1021/acscatal.3c02735

Chemistry Days Young Researcher Symposium (KP2024-YRS): The Effect of a Humidity Gradient on Tensioned Micro-Veneers

Mikko Valkonen[1], Muhammad Awais[1], and Lauri Rautkari[1]

[1]Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems;
Vuorimiehentie 1, 02150 Espoo / P.O. Box 16300, FI-00076 AALTO; Finland

Wood absorbs moisture when it interacts with water in either liquid or vapour form. Moisture absorption is a phenomenon that causes wood to swell and decreases the mechanical properties of this biomaterial [1]. In practice, moisture always propagates into wood constructs; it is impossible to mitigate this issue efficiently without, for example, chemically treating the wood [2]. The wood moisture content should be considered when replacing fossil-based products such as steel and concrete with sustainable materials like wood. Constructs like high-rise wooden buildings require a better understanding of the moisture sorption behaviour of wood under loading conditions because high-rise wooden buildings involve high-stress states.

The moisture sorption behaviour of stressed wood can be studied with long-wave thermal imaging (thermography). Herein, the heat of sorption of timber as it is subject to high relative humidity (RH), such as a 95 % RH under different loading conditions, is analysable. Methodologically, a FLIR E60 (Teledyne FLIR, Wilsonville, OR, USA) thermal camera was used to image Scots pine (*Pinus sylvestris* L.) sapwood micro-veneers of ca. 15 × 48 mm^2 ($w \times l$) and ca. 145.89 ± 2.31 µm ($n = 3$) thickness under a micro-tensile load along the grain. The load (ca. 20 to 30 N) was generated by a Deben Microtest device (Deben UK Ltd., London, UK) by setting the displacement to a constant value of ca. 0.085 mm. Simultaneously, the RH gradient (ca. 2 to nominal 95 %) was created using an initially sealed and later (after ca. 1 h) opened purpose-built drying box with ca. 5.00 l/min N_2 flushing and a RUMED® Climate Chamber 2000 (Rubarth Apparate GmbH, Laatzen, Germany). Some preliminary results of the change in temperature as a function of RH gradient subjection time are depicted in Figure 1.

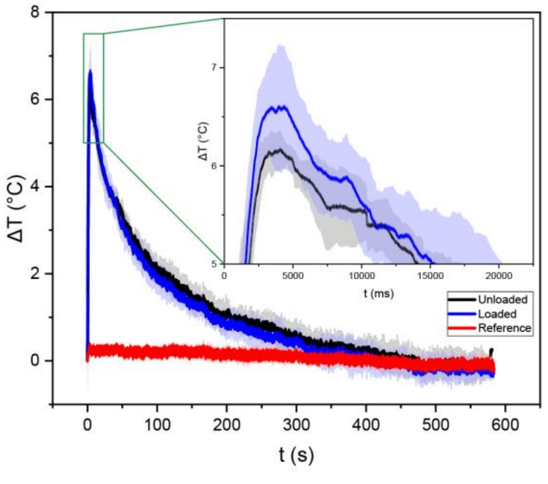

Figure 1: Temperature change as a function of subjection time to the RH gradient. The areas around the plots are the sample standard deviations for the specimens, while $N = 3$ for the specimens and $N = 6$ for the thermally inert reference.

References

[1] Wang, J. Cao, X., Liu, H. *Eur. J. Wood Prod.* 79, (**2021**), 245–59; https://doi.org/10.1007/s00107-020-01623-9.

[2] Lahtela, V. Kärki, T. *Wood Res.-Slovakia* 60 (5), (**2015**), 763–72; http://www.centrumdp.sk/wr/201505/08.pdf.

Chemistry Days Young Researcher Symposium (KP2024-YRS)

Synthesis of novel metallogel and metal complexes using hexa-pyridine triphenylene ligands.

Navdeep Kajal, Rajendhraprasad Tatikonda, and Matti Haukka
[1]Department of Chemistry, University of Jyväskylä, P. O. Box 35, FI-40014 Jyväskylä, Finland
Email : navdeep.n.kajal@jyu.fi

Coordination Polymer Gels (CPGs) constitute a subset of solid-like metal ion and bridging organic ligand structures (like MOFs) that form multi-dimensional networks through a trapped solvent because of non-covalent interactions. The pyridine qualifies as a ligand for transition metals and can form metal complexes with all the metals in the periodic table due to its Lewis basic nature, which is rooted in its nitrogen lone pair. It is typically a weak monodentate ligand that can bind metal in a variety of ratios to form a variety of metal complexes.

In this work, we have synthesized the hexa-pyridine triphenylene ligands by Suzuki coupling reaction, where nitrogen is at meta (Figure 1, I) and para (Figure 1, II) position respectively. The synthesis of ligands is confirmed by both NMR and single crystal X-ray measurements respectively. Thereafter, these ligands were used in the gelation and metal complex formation. From (I) we got a gel with $CuCl_2$ in DMSO. The optimized ratio of ligand to metal is 1:2. We tried with other metal-chlorides also but there was no gelation except $CuCl_2$. The minimum gelation concentration (MGC) is 0.6 % (w/v). On the other hand, from (II), we got a gel from Na_2PdCl_4 in DMF and MCG is 0.3 % (w/v). We also got some metal complexes from (I) with mercury and silver. In addition to this, with (II), we got copper, cadmium and silver metal complexes.

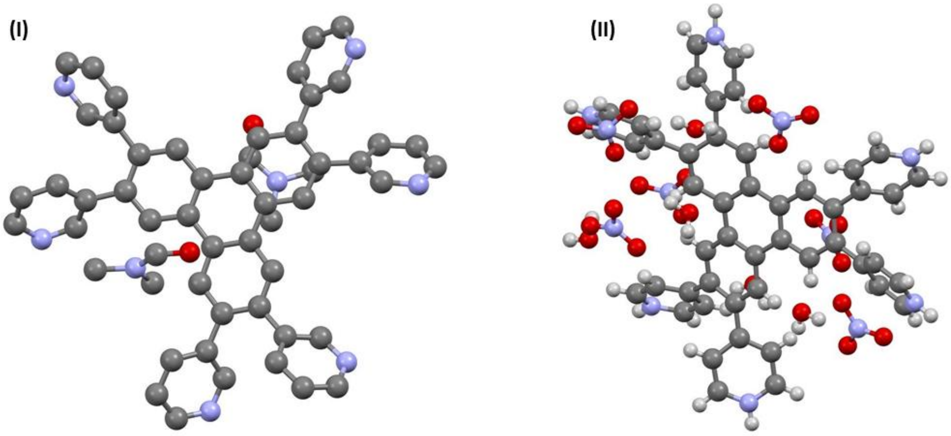

Figure 1 Structure of ligand (I) and protonated version of ligand (II)

Selective Processing of Coinage Metals in Sustainable Ionic Organic Media

Anže Zupanc[1], Joseph Install[1], Timo Weckman[2], Mikko Heikkilä[1], Marianna Kemell[1],
Karoliina Honkala[2], and Timo Repo[1]*

[1]Department of Chemistry, Faculty of Science, University of Helsinki, A. I. Virtasen aukio 1, 00014
Helsinki, Finland

[2]Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, FI-40014
Jyväskylä, Finland

Coinage metals Cu, Ag and Au nowadays prevalently serve as components of industrial and personal electronics. As their natural resources are quickly depleting, their recycling from industrial and urban waste streams will have to heavily support the mineral extraction and replace it in the future. Due to the higher content of metals compared to average ore, recycling of secondary materials could not only become a necessity, but also an economical opportunity. Currently applied dissolution processes are on the other hand burdened with various issues regarding selectivity and environmental impact. Design of new sustainable and selective models is therefore necessary to reach the security of their supply. [1]

Utilization of organic media for dissolution of noble metals can provide a solution for abovementioned sustainability issues, especially when solvents are biomass-based. [2, 3] Induction of selectivity in one, primary dissolution step is on the other hand still a difficult task. Deep eutectic solvents (DES) are a novel type of green ionic media, similar to ionic liquids (ILs): they are affordable, safe and potentially recyclable. [4] With diversity of biomass-based ionic solvents they hold an unexploited potential to become a next generation of sustainable media with inherent opportunity for selectivity.

Herein we present a *one metal – one system* approach for consequent dissolution of single metals from Cu, Ag and Au mixture by changing the type of biomass-based ionic solvent and tuning the strength of the oxidants. We managed to exploit specific metal-ion interactions and difference in oxidation potentials between different metals to induce selectivity in each, primary dissolution stage. This reduced the overall number of processing steps for mixed-metal substrates. To close the recycling loop, pure metals or metal compounds were quantitatively recovered from solutions by employment of green solvents and inexpensive inorganic compounds. Ionic solvents were successfully recycled and reused as dissolution media.

References

[1] A. Zupanc, J. Install, M. Jereb, T. Repo. *Angew. Chem. Int. Ed.* 62, (**2023**), e202214453;
https://onlinelibrary.wiley.com/doi/full/10.1002/anie.202214453
[2] A. Zupanc, E. Heliövaara, K. Moslova, A. Eronen, M. Kemell, Č. Podlipnik, M. Jereb, T. Repo. *Angew. Chem. Int. Ed.* 61, (**2022**), e202117587;
https://onlinelibrary.wiley.com/doi/full/10.1002/anie.202117587
[3] X. Li, K. Binnemans. *Chem. Rev.* 121, (**2021**), 4506;
https://pubs.acs.org/doi/10.1021/acs.chemrev.0c00917
[4] Z. Yuan, H. Liu, W. Fen Yong, Q. She, J. Esteban. *Green. Chem.* 24, (**2022**), 1895;
https://pubs.rsc.org/en/content/articlelanding/2022/gc/d1gc03851f

Trash to Treasure: Recovery of Pt with Impurities in Industrial Process Solutions

Linfan Cui[a,b], Reima Herrala,[a,b] Kirsi Yliniemi[a,b], Jaana Vapaavuori[b], Mari Lundström[a]

[a] Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Espoo 02105, Finland

[b] Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, Espoo 02105, Finland

Concerns about metal scarcity are becoming prevalent due to the depletion of the world's natural resources and increased demand of metal productions. More attention is turned to the recovery of secondary resources. For instance, the process solutions in the final stages of hydrometallurgical or pyro-hydrometallurgical operations still contain precious metals Ag, Au, and platinum group metals at very low concentrations ($< \text{mg L}^{-1}$ or $< \mu\text{g L}^{-1}$). A recently developed electrodeposition-redox replacement (EDRR) method with renewable energy provides not only the basis for sustainable metal recovery but also allows selectively recovery of precious metals from hydrometallurgical process solutions [1]. It has been observed in EDRR that metal reduction may also occur via aqueous reduction close to the electrode with lower energy consumption and higher purity of end-products [2,3]. In current study, an electrochemically aqueous reduction (EAR) method is proposed to recover Pt with the assistance of impurity Fe which typically presents in hydrometallurgical solution. The Fe(III) species in solutions is first reduced to its lower oxidation state Fe(II), and the produced aqueous Fe(II) species is then utilized as reductants to recover dissolved Pt through the redox replacement (Figure 1). As a result, Pt with high purity is successfully recovered on the electrode via EAR, where the deposition rate, energy consumption and morphology of the Pt deposits can be flexibly controlled through operational parameters. The influence of the electrolytes on the EAR process is also investigated, further paving the way to apply the EAR method into other metal recovery systems. In the perspective of materials science, the functional applications of the recovered Pt as electrochemical catalysts are also explored, highlighting the EAR method as a potential recycling solution to contribute to circular economy of critical metal products.

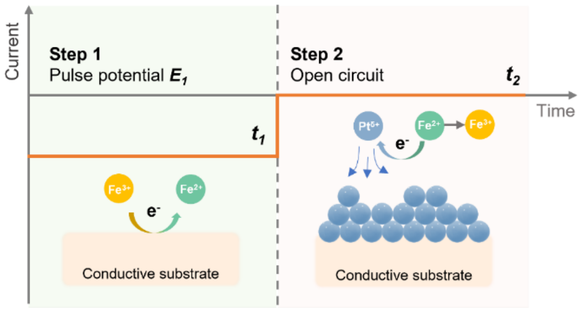

Figure 1. The schematic of EAR process.

Acknowledgements

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Reference

[1] L. Cui, K. Yliniemi, J. Vapaavuori, M. Lundström, Chem Eng J. 465 (2023) 142737.

[2] I. Korolev, S. Spathariotis, K. Yliniemi, B.P. Wilson, A.P. Abbott, M. Lundström, Green Chem. 22 (2020) 3615–3625.

[3] R. Herrala, Z. Wang, J. Vapaavuori, M. Lundström, K. Yliniemi, J Phys Chem C. 127 (2023) 16099–16109.

Thermodynamics of Aqueous Vanadium Solutions

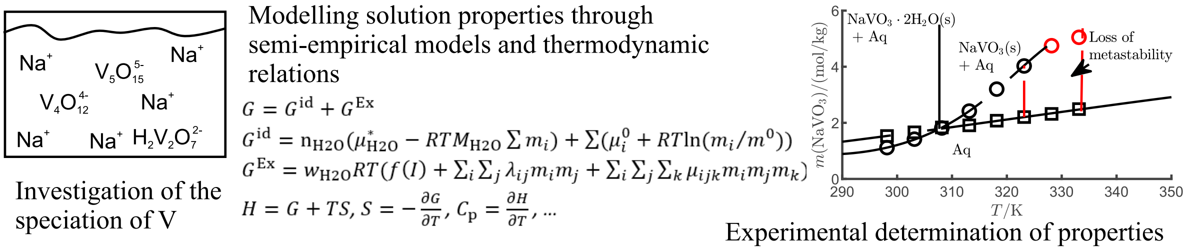
Mikael A. E. Manninen, Tuomas J. Vielma, and Ulla M. Lassi

University of Oulu, Research Unit of Sustainable Chemistry, Pentti Kaiteran katu 1, Finland

Vanadium (V) has been listed as a critical raw material by the European Union as it is used in many fields of modern industry [1,2]. However, the concentration of vanadium in natural deposits is often so small that direct recovery is rarely economical. A more sustainable approach is to recover V from secondary raw materials, such as steel industry slags, utilizing hydrometallurgical unit operations [3]. Quantitative description of equilibrium properties in aqueous vanadium systems would be of great value for the design and control of such processes. Thermodynamic models could also find use in the investigation of the mobility and accumulation of toxic V(V) in the environment.

Unfortunately, the current data for the thermodynamic properties of aqueous V systems is scarce. Therefore, new experimental measurements are needed. Work aiming for the PhD of the first author is centered around this issue. The principal objective of this work is to participate in filling this gap in knowledge by performing accurate measurements of properties, such as solubility [4] and freezing point depression in industrially important aqueous vanadium systems.

This data can be utilized in the development of thermodynamic models capable of predicting the properties of V-bearing solutions in a wide range of conditions. However, the highly nonideal nature of electrolyte solutions and the complex speciation of vanadium makes this a difficult task, as there are many parameters to be determined [4]. In the present work the possibilities to model some industrially relevant binary (e.g., $NaVO_3$–H_2O and NH_4VO_3–H_2O) and ternary systems based on the currently available data are also investigated.



Investigation of the speciation of V

Modelling solution properties through semi-empirical models and thermodynamic relations

$$G = G^{\mathrm{id}} + G^{\mathrm{Ex}}$$

$$G^{\mathrm{id}} = \mathrm{n}_{\mathrm{H2O}}(\mu^{*}_{\mathrm{H2O}} - RTM_{\mathrm{H2O}} \sum m_i) + \sum(\mu_i^0 + RT\ln(m_i/m^0))$$

$$G^{\mathrm{Ex}} = w_{\mathrm{H2O}}RT(f(I) + \sum_i \sum_j \lambda_{ij} m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k)$$

$$H = G + TS, S = -\frac{\partial G}{\partial T}, C_{\mathrm{p}} = \frac{\partial H}{\partial T}, \ldots$$

Experimental determination of properties

Figure 1: Graphical abstract.

References

[1] Proposal for A Regulation of the European Parliament and of the Council of 16 March 2023 establishing a framework for ensuring a secure and sustainable supply of critical raw materials and amending Regulations (EU) 168/2013, (EU) 2018/858, 2018/1724 and (EU) 2019/1020, (COM/2023/160 final). https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52023PC0160.

[2] Moskalyk, R. Alfantazi, A. *Miner. Eng.* 16, (**2003**), 793–805; https://doi.org/10.1016/S0892-6875(03)00213-9.

[3] Lee, J.-C. Kurniawan, Kim, E.-Y. Chung, K. W. Kim, R. Jeon, H.-S. *J. Mater. Res. Technol.* 12 (**2021**), 343-364; https://doi.org/10.1016/j.jmrt.2021.02.065.

[4] Manninen, M.A.E. Vielma, T.J. Lassi, U.M. *J. Chem. Eng. Data.* 68 (**2023**) 2500–2511. https://doi.org/10.1021/acs.jced.3c00367.

Posters:

PO1	Lukas Enders	HU	Novel Chiral Imidazopyridine Au(I)-NHC Complexes for Enantioselective Enyne Cycloisomerizations
PO2	Tigany Zarrouk	Aalto	The Death of XPS Peak Fitting: Unifying Experimental Data with Atomic Structure
PO3	Zahra Madani	Aalto	Heat-Induced Actuator Fibers: Starch-Containing Biopolyamide Composites for Functional Textiles
PO4	Kim Eklund	Aalto	Pyroelectric Effect in Ferroelectric Perovskites Studied with Density Functional Theory
PO5	Mario Mäkinen	Aalto	Modelling the Growth of Zincone ALD/MLD Hybrid Thin Films: a DFT Study
PO6	Mohammed Awashra	Aalto	Superhydrophilic/ Superhydrophobic Droplet Microarrays of Low Surface Tension Biofluids for Nucleic Acid Detection
PO7	Benedikt Gocht	HU	Photooxidation of 3-Bromo-2,5-Dihydrofuran Derivatives to 3(2H)-Furanones
PO8	Kourosh Hasheminejad	Aalto	Designing self-assembling polymeric films by dissipative particle dynamics simulations
PO9	Aydin Bordbar Khiabani	Aalto	Electrochemical Behavior of Ti Implants in Inflammatory Conditions

PO10	Erfan Kimiaei	Aalto/NCSU (USA)	Smart Assembly of Cellulose with Biodegradable Polyesters for Barrier Applications: From Interfacial Design to Lifecycle Assessment and End-life in Aquatic Environments
PO11	Anna Lenarda	HU	Chemically activated Spruce Organosolv Lignin as Carbocatalyst for Heterogeneous Oxidative Dehydrogenations (of N-heterocycles) in Liquid Phase
PO12	Mikael Manninen	UO	Thermodynamics of Aqueous Vanadium Solutions
PO13	Valtteri Oksanen	VTT	Nickel-Electrocatalyzed Synthesis of Bifuran-Based Monomers
PO14	Navdeep Kajal	JYU	Synthesis of novel metallogel and metal complexes using hexa-pyridine triphenylene ligands
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PO18	Elavarasi Sundhararasu	UO	Fixed-bed column studies of heavy metal and ammonium removal by using alkali-activated adsorbent from industrial side streams
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PO21	Sara Lund	ÅA	From Exfoliated Graphite to Graphene-Based Anodes for Sustainable Biophotovoltaic Applications

Chemistry Days Young Researcher Symposium (KP2024-YRS): Novel Chiral Imidazopyridine Au(I)-NHC Complexes for Enantioselective Enyne Cycloisomerizations

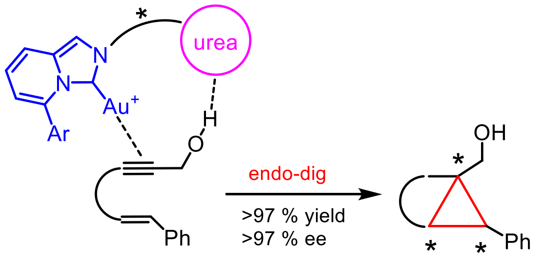
Lukas ENDERS,[a,b] Virginie MOURIÈS-MANSUY,[a] Juho HELAJA,[b] Louis FENSTERBANK[a]

[a] *Sorbonne Université Paris, IPCM, UMR CNRS 8232 – Case 229, Tour 32/42 – 5ème étage, 4 Place Jussieu, 75352 Paris*
[b] *University of Helsinki, A.I. Virtasen aukio 1, 00560 Helsinki, Finland*

Enyne cycloisomerizations are a powerful tool to create complexity within a molecule from easily accessible starting materials. Metallic Lewis acids such as gold, palladium and platinum have been utilized for this type of reactions in recent years, activating unsaturated hydrocarbon bonds for intramolecular cyclization reactions.[1] Establishing Au(I) complexes as enantioselective catalysts presents a special challenge, which is due to the linear coordination sphere and therefore large distances between a chiral ligand and the reactive center.

Pathfinding works by Echavarren and Toste utilize axial chirality to tackle this issue.[2,3] In their case, binaphthyl-based counterions result in high enantioselectivities. Other approaches employ direct phosphine or N-heterocyclic carbene (NHC)-tethered axial chirality as well as cyclodextrin-based ligands, while examples of ligands featuring a single stereocenter are very rare.[4,5]

In our study we show the first example of a chiral, non-symmetric Au(I)-NHC, which is able to perform various enyne cycloisomerization reactions in up to excellent yields and enantioselectivities. The studied complexes utilize an imidazopyridine-based NHC core in combination with a chiral, urea-containing side-arm. We observe tunable selectivity dependent on the urea-moiety as well as unique reactivity due to urea-substrate interactions.



References

1. Cecchini, C.; Cera, G.; Lanzi, M.; Marchiò, L.; Malacria, M.; Maestri, G. *Org. Chem. Front.* **2019**, 6, 3584–3588.
2. Franchino, A.; Martí, À.; Echavarren, A. M. *JACS* **2022**, 144, 3497–3509.
3. Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. *Science (N.Y.)* **2007**, 317, 496–499.
4. Zuccarello, G.; Escofet, I.; Caniparoli, U.; Echavarren, A. M. *ChemPlusChem* **2021**, 86, 1283–1296.
5. Tugny, C.; del Rio, N.; Koohgard, M.; Vanthuyne, N.; Lesage, D.; Bijouard, K.; Zhang, P.; Meijide Suárez, J.; Roland, S.; Derat, E.; Bistri-Aslanoff, O.; Sollogoub, M.; Fensterbank, L.; Mouriès-Mansuy, V. *ACS Catal.* **2020**, 10, 5964–5972.

Chemistry Days Young Researcher Symposium (KP2024-YRS): The Death of XPS Peak Fitting: Unifying Experimental Data with Atomic Structure.

Zarrouk, Tigany[1] and Caro. Miguel[1]

[1]Department of Chemistry and Materials Science, Aalto University, 02150 Espoo, Finland

Interpretation of X-ray Photoelectron Spectroscopy (XPS) spectra is inconsistent, and at worst, a complete fiction. The analysis involves splitting a spectrum of a material into a sum of peaks at reference energies, each of which correspond to certain chemical motifs, with their respective heights giving their proportion in the structure. However, the assumptions on which this analysis relies on, that environments in the material similar to those of the chemical references have similar core electron binding energies, and that these motifs do not contribute at any other part of the spectrum, is generally not the case. We present a general method to produce structures which agree with both experimental and ab-initio data, and demonstrate this. Employing a Machine-Learned XPS model built on GW and Density Functional Theory (DFT) data, in conjunction with a CO Gaussian Approximation Potential (GAP), we performed modified Grand-Canonical Monte-Carlo simulations to obtain low-energy oxygenated amorphous carbon structures which agree with experimental XPS data. As expected, numerous low-energy structures are able to fit the spectra, with structural motifs contributing at a range of core electron binding energies over the spectra, see figure 1. We also show the results of "generalised dynamics" by extending the Hamiltonian to include the influence of XPS data on the forces, allowing for experimental agreement simply by performing molecular dynamics. All of these features are implemented within the TurboGAP code.

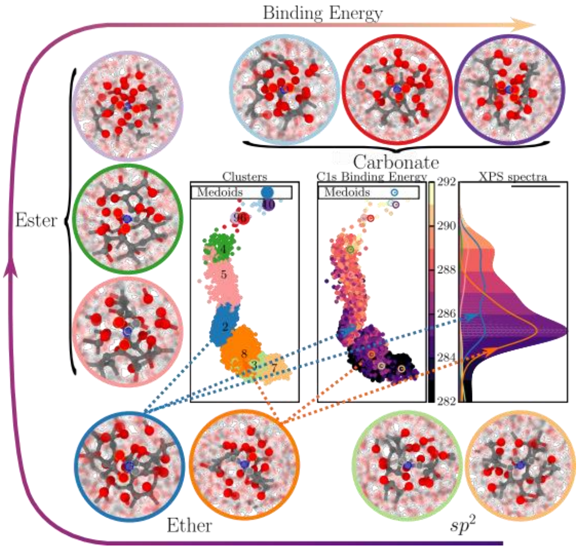


Figure 1: Cluster MDS embedding of atomic environments, with the representative environment of the clusters coloured according to the clustering on the left. Middle, points coloured by the predicted core electron binding energy. Right, contributon to the final XPS structure shown by the coloured lines.

PO3

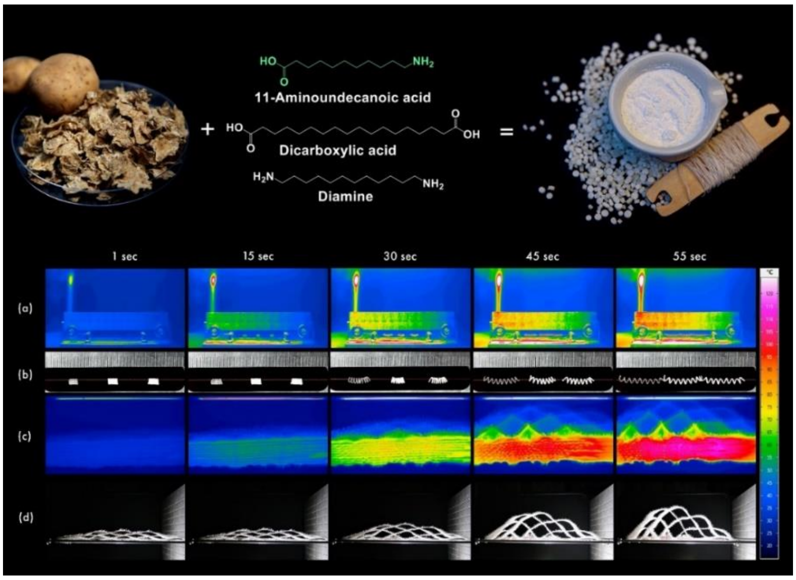
Heat-Induced Actuator Fibers: Starch-Containing Biopolyamide Composites for Functional Textiles

Zahra Madani[1], Hossein Baniasadi[2], Mithila Mohan[1], Maija Vaara[1], Sami Lipponen[2], Jaana Vapaavuori[1]*, Jukka V. Seppälä[2]*

[1]Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, Kemistintie 1, 02150, Espoo, Finland.

[2]Polymer Technology, School of Chemical Engineering, Aalto University, Kemistintie 1, 02150, Espoo, Finland.

The importance of smart textiles lies in their ability to surpass the limitations of conventional textiles, introducing advanced functionalities to diverse needs across various industries. The significance of shape-changing fabric stems from its transformative functionalities applicable across various industries, revolutionizing design and user experience, particularly in fashion, healthcare, and robotics. The innovative materials facilitate adaptive structure and dynamic forms, demonstrating versatility in adapting to changing needs and environments. In this work, we studied the development of a thermally responsive shape-changing fabric using a self-synthesized low-melting point polyamide/starch shape-memory polymer actuator. Additionally, we present a straightforward and solvent-free method for the compatibilization of starch particles with the synthesized bio-polyamide, aiming to enhance the sustainability of polyamide and customize the actuation temperature. The resulting bio-based polymer composites exhibit excellent mechanical properties (Tensile modulus up to 872 MPa) comparable to those reported for soft and tough materials, making them well-suited for textile integration. To demonstrate the potential application of using biocomposites in textiles, a heat-responsive fabric was created using thermo-responsive shape memory polymer actuators composed of a biocomposite containing 50 wt.% compatible starch. This fabric shows the ability to repeatedly undergo significant heat-induced deformations by opening and closing pores, thereby exposing hidden functionalities through heat stimulation. This innovative approach provides a convenient pathway for designing heat-responsive textiles, adding value to state-of-the-art smart textiles.



PO4

Pyroelectric Effect in Ferroelectric Perovskites Studied with Density Functional Theory

Kim Eklund[1] and Antti J. Karttunen[1]

[1]Department of Chemistry and Materials Science, Aalto University

Ferroelectric perovskites such as $BaTiO_3$, $KNbO_3$, and $PbTiO_3$ and various solid solutions based on them are important functional materials in electrical engineering and related applications. In the pyroelectric effect, exhibited by all ferroelectrics, the spontaneous polarization of the polar material changes upon temperature fluctuation. This electric polarization is extractable as a current. Pyroelectrics are used in various sensor applications and other electronics, but also show potential for waste heat harvesting and catalysis applications. Measurement of the pyroelectric effect is rather complicated experimentally, and computational tools could aid in the design of novel pyroelectrics by providing an accurate route to modelling and screening of the pyroelectric properties.

We have developed a computational methodology, based on density functional theory (DFT), self-consistent phonon calculations (SCPH), and Berry phase theory of polarization, to evaluate the primary pyroelectric coefficient of tetragonal-structured perovskite ferroelectrics at finite temperatures [1]. The total pyroelectric coefficient consists of two parts, primary and secondary, where the secondary effect is a piezoelectric contribution. This too, can be evaluated with quasi-harmonic approximation (QHA) combined with the calculation of elastic and piezoelectric constants. Results obtained for $BaTiO_3$ show reasonable agreement with experimentally measured values, indicating that the supercell-based methodology can further be used for known and predicted perovskite solid solutions.

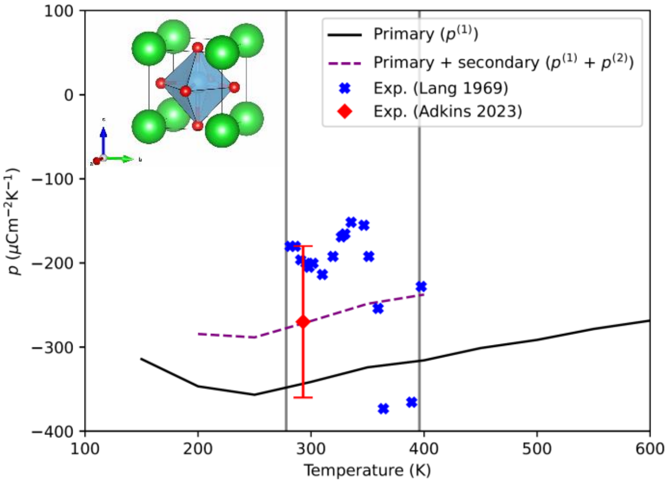


Figure 1: Pyroelectric coefficient of $BaTiO_3$ at finite temperatures calculated with DFT.

References

[1] Eklund, K., Karttunen A. J., *J. Phys. Chem. C.* (**2023**), accepted.

Modelling the Growth of Zincone ALD/MLD Hybrid Thin Films: a DFT Study

M. Mäkinen, and K. Laasonen

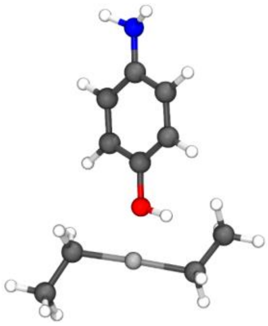
Aalto University School of Chemical Engineering, Kemistintie 1, 02150 Espoo, Finland

Purely inorganic, or organic thin films can be fabricated using either atomic or molecular layer deposition (ALD and MLD). By combining these two methods, one can fabricate hybrid thin films, which contain both organic and inorganic layers, and thus will drastically improve the applicability of the thin film technology. Future applications of these hybrid thin films include electrode and coating materials for battery applications, solar cells, UV-active photoluminescence materials, protective coatings, catalytic applications, and flexible lightweight magnets. [1] The reaction mechanisms of the growth process of hybrid thin films are mostly unknown. However, adsorption reactions used to fabricate these hybrid materials can be studied using density functional theory (DFT) -modelling, and thus we can reveal the chemistry occurring in the reactor during the thin film deposition process.

Hybrid thin films under investigation are fabricated using diethyl zinc and an organic bifunctional aromatic precursor, which was either 4-aminophenol or hydroquinone, as precursors. These thin films were studied using gas-phase and surface reaction models, of which examples are presented in Figure 1. The surface models consisted of an ethyl-saturated zinc oxide surface and the adsorbing organic precursor 4-aminophenol.

Modelling of the reaction pathways was conducted using the GPAW program. DFT was used with Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional. Van der Waals correction TS09 was used due to weak interactions caused by the ethyl ligands All the reaction barriers were calculated using the nudged elastic band -method with a climbing image.

4-aminophenol reacts more strongly with its hydroxyl than its amino group. It adsorbed to the surface through exothermic physisorption, and after that more strongly using either ligand-exchange or dissociation reaction. The key step of the total reaction is the removal of the ethyl group as ethane. We have identified multiple ethyl removal processes on the interface between the layer of 4-aminophenol and zinc oxide, and that they depend on the coverage of ethyl ligands on the zinc oxide surface.



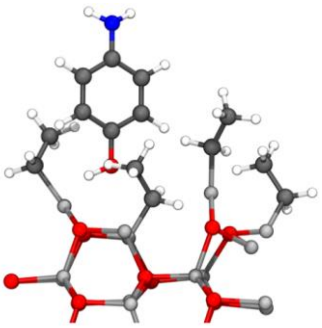


Figure 1: Initial state of a hybrid thin film growth reaction in gas-phase (left) and surface model (right).

References

[1] Multia, J. Karppinen, M. *Adv. Mater. Interfaces*. 9 (15), **(2022)**, 2200210; https://doi.org/10.1002/admi.202200210

Superhydrophilic/ Superhydrophobic Droplet Microarrays of Low Surface Tension Biofluids for Nucleic Acid Detection

M. Awashra[1], P. Elomaa[2], P. Saavalainen[2], V. Jokinen[1]
[1]Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, 02150 Espoo, Finland mohammad.awashra@aalto.fi ville.p.jokinen@aalto.fi
[2]Translational Immunology Research Program and Department of Medical and Clinical Genetics, Faculty of Medicine, University of Helsinki, Haartmaninkatu 8, Helsinki 00290, Finland

Many diseases can be identified by analyzing the nucleic acid of the microbe or virus causing the disease. Polymer Chain Reaction (PCR) is currently the gold standard for nucleic acid detection. However, this method has some challenges such as their dependence on relative quantification, which necessitates external calibration using genetic standards. Digital PCR (dPCR) is a detection technique that overcomes this challenge. Its principle is the partitioning of the tested sample into exceedingly small droplets that can have one or zero copy of the target RNA. Then by having separate amplification reactions in each droplet, the droplets that have the target RNA will show a positive fluorescent signal. By counting the number of fluorescent droplets, one can know the number of RNA copies in the sample. Currently, the commercial method used to partition a sample into small droplets is droplet microfluidics where the droplets are in an immiscible liquid (oil). This method requires constant pumping and the use of surfactants. Moreover, the cross contamination between the droplets is a potential risk.

This study reports a different method for sample partitioning. Which is based on the difference of hydrophilicity (affinity for water) between two regions on a given surface. We have fabricated a black silicon surface with circular spots that are superhydrophilic (SHL) (extremely high affinity for water) and these spots are surrounded with a superhydrophobic (SHB) (almost no affinity for water) regions. This extreme difference in wettabilities between the two regions forms water droplets on the superhydrophilic spots. Here, we utilize this droplet microarray platform for dPCR using droplet digital strand invasion-based amplification (ddSIBA) technology. The black silicon was formed by etching technology and then it was patterned to SHL spots and SHB regions by changing the surface chemistry using lithography. Then, to overcome the challenge of low surface tension in SIBA mixture, a protective oil coating method was developed to prevent the SIBA mixture from being adsorbed on the SHB regions as shown in **Figure 1a**. Using this method, the SIBA mixture sample was successfully partitioned into droplets on the SHL spots and separated by the SHB borders and protective oil coating [1].

Nucleic acid detection experiments with varying COVID-19 virus RNA concentrations were performed using ddSIBA. The results are shown in **Figure 1b** and suggest a strong linear relationship between the expected and measured RNA copy numbers showing that ddSIBA on our platform is quantified [1].

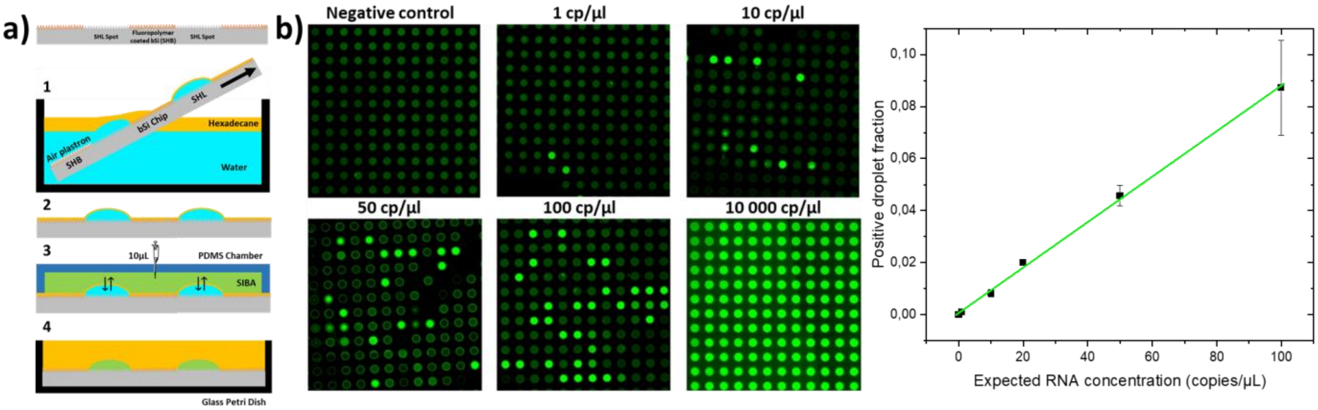


Figure 1. a) The workflow of the strand invasion-based amplification (SIBA) mixture droplet microarray formation. b) Left: Fluorescent images of the ddSIBA quantification experiment performed with SARS-CoV-2 RNA concentrations ranging from 0 to 10 000 copies/µL using our platform. Right: Strong linear correlation between the counted positive droplets and expected RNA concentration [1].

References

[1] M. Awashra, P. Elomaa, T. Ojalehto, P. Saavalainen, and V. Jokinen. **Superhydrophilic/ Superhydrophobic Droplet Microarrays of Low Surface Tension Biofluids for Nucleic Acid Detection,** Adv. Mater. Interface. *In Press*, **2023.**

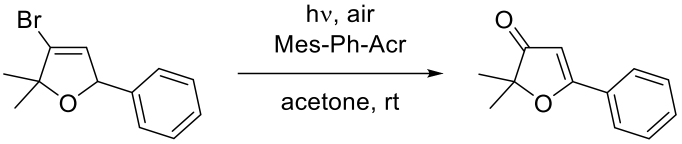
PO7

Photooxidation of 3-Bromo-2,5-Dihydrofuran Derivatives to 3(*2H*)-Furanones

Benedikt Gocht[1], Janne M. Naapuri[1], and Jan Deska[1]

[1]Department of chemistry, University of Helsinki, A. I. Virtasen aukio 1, 00560 Helsinki, Finland

Recent decades have seen an increased interest in photochemical reactions, as they are useful complementary tools besides thermally driven chemistry, enabling transformations in mild conditions that are not attainable using traditional methods. [1, 2] In this work the photocatalytic oxidation of 3-bromo-2,5-dihydrofuran (**1**) to 3(*2H*)-furanone (bullatone, **2**) and their derivatives using aerial oxygen and an organic photocatalyst was investigated.



1

bullatenone (**2**)

Figure 1: The photooxidation investigated in this work.

The substrate scope of this reaction was probed, focusing on the 2- and 5-position. Mechanistic studies were carried out utilizing kinetic measurements on selected substrates, Hammett analysis, kinetic isotope effect, an ^{18}O-marking experiment, as well as superoxide and intermediate trapping.

As the presented photocatalytic transformation utilizes light as its energy source, molecular oxygen from the air as the oxidant, a non-metal based photocatalyst in acetone, it can be considered a very environmentally benign process. [3] Understanding this reaction in detail is of great value, as it potentially presents a more sustainable way to access functionalized structures containing the bullatenone-framework, such as the bioactive compounds polmacoxib or biyouyanagin A.

References

[1] Mai, S., González, L. *Angew. Chem. Int. Ed.* 59 (39), (**2020**), 16832; https://doi.org/10.1002/anie.201916381

[2] Joshi-Pangu, A., Lévesque, F., Roth, H.G., Oliver, S.F., Campeau, L.C., Nicewicz, D., DiRocco, D.A. *J. Org. Chem.* 81 (16), (**2016**), 7244; https://doi.org/10.1021/acs.joc.6b01240

[3] Anastas, P.T., Warner, J.C. *Green chemistry. Theory and practice.* Oxford University Press, Oxford (**1998**)

Designing self-assembling polymeric films by dissipative particle dynamics simulations

Kourosh Hasheminejad[1,2], Alberto Scacchi[1,2], Sousa Javan Nikkhah[3], and Maria Sammalkorpi[1,2,4]
[1]Department of Chemistry and Materials Science, Aalto University, Finland
[2]Academy of Finland Center of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, Finland
[3]Department of Chemical Sciences, Bernal Institute, University of Limerick, Republic of Ireland
[4]Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland
Email: kourosh.hasheminejad@aalto.fi / WWW: https://www.aalto.fi/en/department-of-chemistry-and-materials-science/soft-materials-modelling

Interfacial coatings by, e.g., polymers, are often used to modify surface interactions of materials, or to protect the underlying substrate. Self-assembling polymer coatings find use e.g., as protective layers in biomedical applications, as anti-corrosion coats protecting metallic surfaces, but also as preservative layers conserving stone materials in architectural monuments. Advanced uses require control of the assembling structure and coating spreading. Computational modelling provides an effective means to reveal guidelines for these, e.g., in terms of polymer component choices, their miscibilities, or degree of polymerization.

Here, we employ dissipative particle dynamics (DPD) simulations to study the self-assembly of protective polymeric coatings and their structures. We focus on a model system composed of a hydrophilic surface coated via self-assembly of linear amphiphilic di-block copolymers and linear hydrophobic polymers. The model substrate matches cellulose, while the hydrophilic segments represent starch, and the hydrophobic material a random co-polymer of styrene and n-butyl acrylate (at equal weight ratio). Our results show that copolymers with equal block lengths form stable, well-ordered lamellar surface coatings, while block length asymmetry leads to advanced patterning in the coating. We examine the effect of concentration, extracting coating spreading and optimal concentration trends for uniform complete coatings, and map the sensitivity of the assembly to chemical composition by varying the DPD interaction parameters. Our work provides guidelines for tuning and controlling the self-assembly of polymeric coatings and their internal structures for surface modifying applications.

References

[1] Kourosh Hasheminejad, Alberto Scacchi, Sousa Javan Nikkhah, and Maria Sammalkorpi. "Cracking polymer coatings of paper-like surfaces: Control via block co-polymer structure and system composition." Applied Surface Science 640 (2023): 158324. https://doi.org/10.1016/j.apsusc.2023.158324
[2] Alberto Scacchi, Kourosh Hasheminejad, Sousa Javan Nikkhah, and Maria Sammalkorpi. "Controlling self-assembling co-polymer coatings of hydrophilic polysaccharide substrates via co-polymer block length ratio." Journal of Colloid and Interface Science 640 (2023): 809-819. https://doi.org/10.1016/j.jcis.2023.02.117

PO9

Electrochemical Behavior of Ti Implants in Inflammatory Conditions

Aydin Bordbar Khiabani and Michael Gasik

CMET Department, School of Chemical Engineering, Aalto University, Espoo, Finland

This extensive study explores the significant impact of inflammation on the electrochemical corrosion of metallic implants, which can compromise their integrity and function, often leading to foreign body reactions [1]. To mitigate these issues, the research introduces the promising Ti-Nb-Zr-Si (TNZS) alloy and assesses its electrochemical performance against Ti2 and Ti23 alloy. The results reveal TNZS's superior corrosion resistance, making it an attractive material for orthopedic applications, with cell culture investigations demonstrating favorable biocompatibility compared to Ti23. The study emphasizes the importance of understanding biomaterial electrochemical behavior, particularly in metals susceptible to oxidation and corrosion under various conditions [2]. Furthermore, the research delves into the electrochemical behavior of 3D patterned Ti2 and Ti23 alloys, showing improved corrosion resistance with longer immersion times. Inflammatory conditions (pH 5) lead to a decline in passive layer resistance due to H_2O_2, while severe inflammation (pH 3) sees albumin, lactate, and H_2O_2 collaboratively diminishing corrosion resistance. Electrochemical impedance data suggests localized pitting in severe inflammatory conditions, altering the transport of corrosive species. 3D Ti alloys exhibit enhanced corrosion resistance compared to untreated Ti (flat) with similar composition due to changes in surface topography and wettability [3]. The application of smart hydrogels on Ti alloys is also explored, offering potential advancements in implant materials [4]. Alginate (Alg) hydrogels, both with and without octacalcium phosphate (OCP), were developed and found to enhance corrosion resistance, particularly with OCP in biological media. Although corrosion resistance decreased in inflammatory conditions, the hydrogel coatings effectively shifted the corrosion potential towards nobler values, reducing corrosion in all conditions. Including OCP particles enhanced electrical charge transfer resistance at the substrate-coating interface, underscoring their potential as advanced implant materials [5].

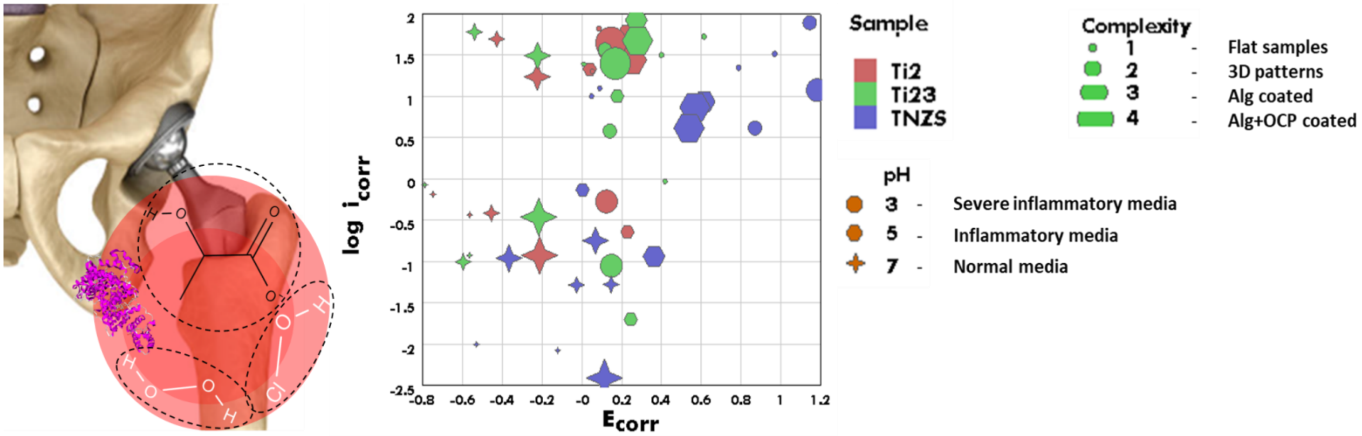


Figure 1: Inflammation after implantation and augmented imputed data analyses for electrochemical studies.

References

[1] Bordbar-Khiabani A, Bahrampour S, Mozafari M, Gasik M. *Ceramics International*. **2022**; 48(3):3148-56.
[2] Bordbar-Khiabani A, Gasik M. *Scientific Reports*. **2023**;13(1):2312.
[3] Bordbar-Khiabani A, Gasik M. *Journal of Materials Research and Technology*. **2023**; 26:356-70.
[4] Bordbar-Khiabani A, Gasik M. *International Journal of Molecular Sciences*. **2022**; 23(7):3665.
[5] Bordbar-Khiabani A, Kovrlija I, Locs J, Loca D, Gasik M. *International Journal of Molecular Sciences*. **2023**; 24(17):13135.

Smart Assembly of Cellulose with Biodegradable Polyesters for Barrier Applications: From Interfacial Design to Lifecycle Assessment and End-life in Aquatic Environments

Erfan Kimiaei[1,2], Nathalie Lavoine[2], Richard Venditti[2], Monika Österberg[1]*

[1]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo, Finland

[2]Department of Forest Biomaterials, College of Natural Resources, North Carolina State University, Raleigh, United States

Natural and biodegradable polymers like cellulose have shown great potential to replace fossil-based plastics. However, its susceptibility to water and moisture poses challenges when blending with hydrophobic polymers, thereby limiting its widespread use. To address these problems, we innovatively introduced the Pickering emulsion as a versatile template for combining hydrophilic nanocellulose with hydrophobic polyesters such as polycaprolactone (PCL) with the help of lignin nanoparticles (LNPs) as an interfacial compatibilizer. Combining LNPs with nanocellulose enabled the production of an ultra-stable PCL emulsion. After drying the emulsion, free-standing composite films with an even dispersion of PCL onto the surface of the nanocellulose network were achieved. The composites exhibited unprecedented mechanical properties in both dry and wet states (tensile strength up to 200MPa and 87MPa, respectively) due to the favorable intercomponent interactions. This interfacial design conferred additional properties to nanocellulose such as great protection against water vapor, UV, and oxidation, making it outstanding for the packaging application. Furthermore, the composite films exhibited excellent biodegradability between 85% and 97% after 42 days of exposure to natural seawater and simulated freshwater. Thus, this interfacial strategy offers a facile route to design multifunctional cellulose-based composites using only lignocellulosic and biodegradable polymers without any chemical modifications that harness the natural biodegradability and maximum benefit of each constituent. In the end, from a sustainability perspective, the life cycle assessment (LCA) of such biocomposite was conducted to evaluate the environmental impacts associated with biocomposite production in comparison with productions of low-density polyethylene (LDPE), a common fossil-based material in the packaging industry. Furthermore, a production hotspot was identified to determine in which scenarios the biocomposite could be a more environmentally friendly alternative than LDPE films within their well-established technology. This information is crucial to help the industry fill the gap in replacing traditional plastics by biobased products with a sustainable approach.

PO11

Chemically activated Spruce Organosolv Lignin as Carbocatalyst for Heterogeneous Oxidative Dehydrogenations (of N-heterocycles) in Liquid Phase

Anna Lenarda,[a] Michele Melchionna,[b] Paolo Fornasiero, [b] Michael Hummel,[c] and Juho Helaja*[a]

[a]Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O. Box 55, 00014 Helsinki, Finland;
[b]Department of Chemical and Pharmaceutical Sciences, INSTM, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy
[c]Department of Bioproducts and Biosystems, Aalto University, Vuorimiehentie 1, 02150 Espoo, Finland

Activated carbons obtained from organosolv lignin by chemical activation with KOH and oxidized with diluted HNO_3 were studied as catalysts for aerobic oxidative dehydrogenation (ODH) reactions. The structure/activity relationship was investigated through multiple techniques revealing the crucial role of specific pore size and oxygen functionalities distribution in promoting two mechanistically archetypical ODH probe reactions: 1) the tetrahydroquinoline (THQ) aromatization, which represents ODH triggered by hydride transfer and 2) the 2-phenyl indole homocoupling reaction, a model for single electron transfer (SET) promoted reactions. In particular, the catalytic activity, correlating with oxygen functionalities distribution on the basis of X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) analysis, was associated with the C=O surface functionalities, as confirmed by blocking experiments with 2,2,2-trifluoroethyl hydrazine. Kinetic profiling tools were employed to assess THQ ODH product inhibition effects on the overall yield of the process as well as the extent of stoichiometric activity of the carbocatalyst. The breadth of the developed catalysts' applicability was explored through selected relevant ODH reactions.

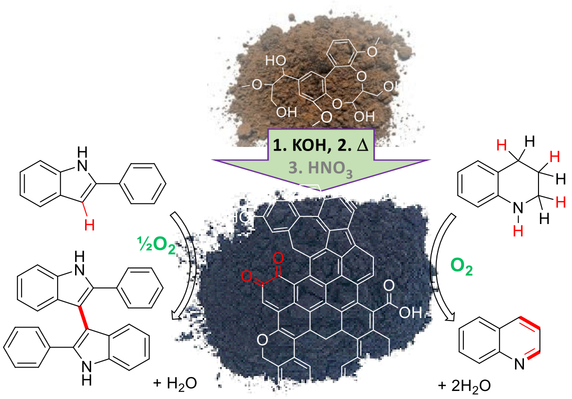


Figure 1: Graphical representation of the catalytic system proposed for the two model reactions explored in this work

References

[1] Lenarda, A.; Melchionna, M.; Aikonen, S.; Montini, T.; Fornasiero, P.; Hu, T.; Hummel, M.; Helaja J.; *ACS Catal.* 13 (17), (**2023**), 11362; https://doi.org/10.1021/acscatal.3c02735

Thermodynamics of Aqueous Vanadium Solutions

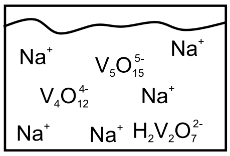
Mikael A. E. Manninen, Tuomas J. Vielma, and Ulla M. Lassi

University of Oulu, Research Unit of Sustainable Chemistry, Pentti Kaiteran katu 1, Finland

Vanadium (V) has been listed as a critical raw material by the European Union as it is used in many fields of modern industry [1,2]. However, the concentration of vanadium in natural deposits is often so small that direct recovery is rarely economical. A more sustainable approach is to recover V from secondary raw materials, such as steel industry slags, utilizing hydrometallurgical unit operations [3]. Quantitative description of equilibrium properties in aqueous vanadium systems would be of great value for the design and control of such processes. Thermodynamic models could also find use in the investigation of the mobility and accumulation of toxic V(V) in the environment.

Unfortunately, the current data for the thermodynamic properties of aqueous V systems is scarce. Therefore, new experimental measurements are needed. Work aiming for the PhD of the first author is centered around this issue. The principal objective of this work is to participate in filling this gap in knowledge by performing accurate measurements of properties, such as solubility [4] and freezing point depression in industrially important aqueous vanadium systems.

This data can be utilized in the development of thermodynamic models capable of predicting the properties of V-bearing solutions in a wide range of conditions. However, the highly nonideal nature of electrolyte solutions and the complex speciation of vanadium makes this a difficult task, as there are many parameters to be determined [4]. In the present work the possibilities to model some industrially relevant binary (e.g., $NaVO_3$–H_2O and NH_4VO_3–H_2O) and ternary systems based on the currently available data are also investigated.



Investigation of the speciation of V

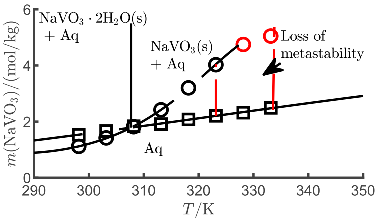
Modelling solution properties through semi-empirical models and thermodynamic relations

$$G = G^{\mathrm{id}} + G^{\mathrm{Ex}}$$

$$G^{\mathrm{id}} = \mathrm{n}_{\mathrm{H2O}}(\mu^{*}_{\mathrm{H2O}} - RTM_{\mathrm{H2O}}\sum m_i) + \sum(\mu_i^0 + RT\ln(m_i/m^0))$$

$$G^{\mathrm{Ex}} = w_{\mathrm{H2O}}RT(f(I) + \sum_i\sum_j \lambda_{ij}m_im_j + \sum_i\sum_j\sum_k \mu_{ijk}m_im_jm_k)$$

$$H = G + TS, S = -\frac{\partial G}{\partial T}, C_{\mathrm{p}} = \frac{\partial H}{\partial T}, \ldots$$



Experimental determination of properties

Figure 1: Graphical abstract.

References

[1] Proposal for A Regulation of the European Parliament and of the Council of 16 March 2023 establishing a framework for ensuring a secure and sustainable supply of critical raw materials and amending Regulations (EU) 168/2013, (EU) 2018/858, 2018/1724 and (EU) 2019/1020, (COM/2023/160 final). https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52023PC0160.

[2] Moskalyk, R. Alfantazi, A. *Miner. Eng.* 16, (**2003**), 793–805; https://doi.org/10.1016/S0892-6875(03)00213-9.

[3] Lee, J.-C. Kurniawan, Kim, E.-Y. Chung, K. W. Kim, R. Jeon, H.-S. *J. Mater. Res. Technol.* 12 (**2021**), 343-364; https://doi.org/10.1016/j.jmrt.2021.02.065.

[4] Manninen, M.A.E. Vielma, T.J. Lassi, U.M. *J. Chem. Eng. Data.* 68 (**2023**) 2500–2511. https://doi.org/10.1021/acs.jced.3c00367.

Nickel-Electrocatalyzed Synthesis of Bifuran-Based Monomers

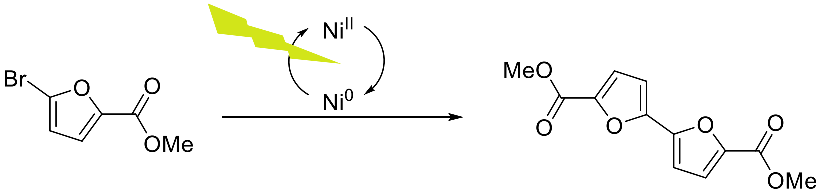
Valtteri Oksanen[1], Sari Rautiainen[1], and Tom Wirtanen[1]

[1]Chemical & Polymer Synthesis, VTT Technical Research Centre of Finland, 02044 Espoo, Finland

More sustainable alternatives are needed for high-volume chemicals such as polymers due to climate change and increasing greenhouse gas emissions. One of the most potential new materials are furan-based polymers, such as polyethylene furan-2,5-dicarboxylate (PEF), which has been envisioned as a replacement for polyethylene terephthalate (PET) and is obtained from lignocellulosic biomass. Considerably less research has been devoted to the synthesis and polymerization of bifurans. These derivatives are readily obtained from hemicellulose, the second most abundant polysaccharide, and they display interesting complementary material properties, as a sole monomer or co-monomer in PEF, such as increased UV resistance, glass transition temperature and O_2 barrier properties compared to PEF.[1]

The synthesis of bifurans is unfortunately far less established than PEF monomers. One of the most viable routes is the homocoupling of bromo furan carboxylates, but the literature methods have some major drawbacks, such as expensive palladium catalysts, and poisonous CO or metal powders as reductants.[2, 3] In this respect, nickel-electrocatalyzed reductive homocoupling of aryl bromides would be an interesting alternative as it would allow to use more inexpensive catalyst and circumvent the need for stoichiometric reductants with electrons. However, the current literature examples employ a sacrificial anode which makes this method as problematic as using stoichiometric metal powders as reductants. Moreover, the nickel-electrocatalyzed synthesis of bifurans has not been described previously in the literature.

We have recently developed reaction conditions for reductive nickel-electrocatalysis particularly suitable for the synthesis bifuran-based monomers.[3] The method circumvents the use of sacrificial anode by utilizing triethanolamine oxidation as the anodic counter reaction and is performed in an undivided cell with graphite electrodes. The method can be extended to bithiophene and biaryl monomers as well, and in all cases, the product separation is achieved effortlessly by precipitation with water. Scale-up studies indicate that the developed method could be used for larger scale synthesis of 2,2-bifuran-5,5-dicarboxylic acid monomer, paving the way for sustainable synthesis of these key monomers.



References

[1] a) Kainulainen, T.P. Hukka, T.I. Özeren, H.D. Sirviö, J.A. Hedenqvist, M.S. Heiskanen, J.P. *Biomacromolecules*, 21 (2), (**2020**), 743–752; https://doi.org/10.1021/acs.biomac.9b01447 b) Kainulainen, T.P. Parviainen, T.A.O. Sirviö, J.A. McGeachie, L.J.R. Heiskanen, J.P. *ACS Macro Lett.* 12 (2), (**2023**), 147–151; https://doi.org/10.1021/acsmacrolett.2c00743

[2] a) Lee, K. Lee, P.H. *Tetrahedron Lett.* 49 (27), (**2008**), 4302–4305; https://doi.org/10.1016/j.tetlet.2008.04.123 b) Zhu, J. Lei, Y. Chen, Z. Liao, Y. Yin, G. *Mol. Catal*. 513 (**2021**), 111814, https://doi.org/10.1016/j.mcat.2021.111814

[3] Oksanen, V. Rautiainen, S. Wirtanen, T. *Chem. Eur. J.* (**2023**), e202302572, https://doi.org/10.1002/chem.202302572

Chemistry Days Young Researcher Symposium (KP2024-YRS)

Synthesis of novel metallogel and metal complexes using hexa-pyridine triphenylene ligands.

Navdeep Kajal, Rajendhraprasad Tatikonda, and Matti Haukka
[1]Department of Chemistry, University of Jyväskylä, P. O. Box 35, FI-40014 Jyväskylä, Finland
Email : navdeep.n.kajal@jyu.fi

Coordination Polymer Gels (CPGs) constitute a subset of solid-like metal ion and bridging organic ligand structures (like MOFs) that form multi-dimensional networks through a trapped solvent because of non-covalent interactions. The pyridine qualifies as a ligand for transition metals and can form metal complexes with all the metals in the periodic table due to its Lewis basic nature, which is rooted in its nitrogen lone pair. It is typically a weak monodentate ligand that can bind metal in a variety of ratios to form a variety of metal complexes.

In this work, we have synthesized the hexa-pyridine triphenylene ligands by Suzuki coupling reaction, where nitrogen is at meta (Figure 1, I) and para (Figure 1, II) position respectively. The synthesis of ligands is confirmed by both NMR and single crystal X-ray measurements respectively. Thereafter, these ligands were used in the gelation and metal complex formation. From (I) we got a gel with $CuCl_2$ in DMSO. The optimized ratio of ligand to metal is 1:2. We tried with other metal-chlorides also but there was no gelation except $CuCl_2$. The minimum gelation concentration (MGC) is 0.6 % (w/v). On the other hand, from (II), we got a gel from Na_2PdCl_4 in DMF and MCG is 0.3 % (w/v). We also got some metal complexes from (I) with mercury and silver. In addition to this, with (II), we got copper, cadmium and silver metal complexes.

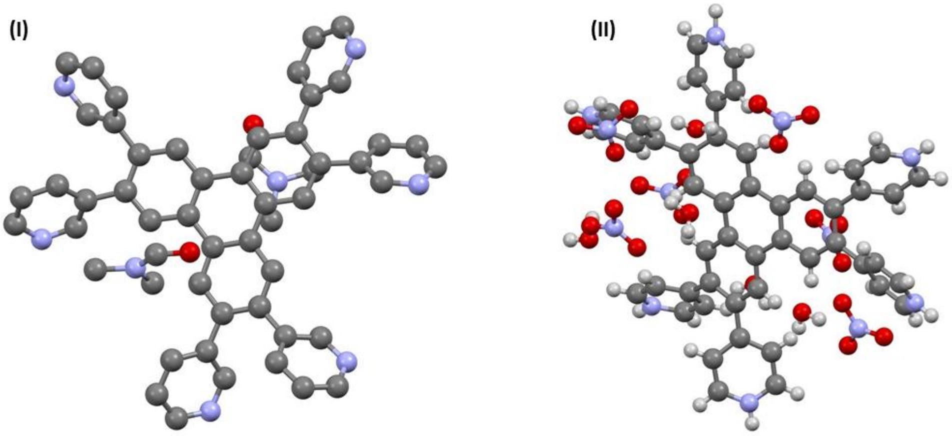


Figure 1 Structure of ligand (I) and protonated version of ligand (II)

A computational approach to carbene-metal-amide OLED materials

Nguyen Le Phuoc[1], Alexander Romanov[2], and Mikko Linnolahti[1]

[1]Department of Chemistry, University of Eastern Finland, FI-80101 Joensuu, Finland

[2]Department of Chemistry, University of Manchester, Oxford Rd., Manchester M13 9PL, UK

Two-coordinate coinage metal complexes are promising materials suitable for utilization in organic light-emitting diode (OLED) devices. This assertion is attributed to their capacity to achieve photoluminescence (PL) quantum yields (PLQY) at unity, arising from either phosphorescence or thermally activated delayed fluorescence (TADF). [1], [2], [3]

Aiming to systematically investigate their PL properties, we conducted a density functional theory study encompassing over 60 gold-centered carbene–metal–amides (CMAs) with a diverse array of cyclic (alkyl)(amino)carbenes (CAACs). Computational findings reveal that these CMAs exhibit efficient TADF behavior when a compromise is attained between oscillator strength coefficient and exchange energy between the lowest excited singlet (S_1) and triplet (T_1) states. These parameters are strongly correlated with vertical S_0-S_1 and S_0-T_1 excitation energies as well as HOMO-LUMO overlap integral, where the HOMO is primarily localized on the amide and the LUMO along the metal–carbene bond. The complexes adopt a nearly coplanar geometry of carbene and amide ligands in the S_0 and T_1 states, whereas they undergo a rotation to a perpendicular orientation in the S_1 state. This geometric transformation is accompanied by a reduction in the S_1-S_0 oscillator strength, which diminishes from its maximal value at coplanar geometry to an approximate null value at rotated geometry. [4]

Guided by calculated results, a novel CMA complex, denoted as (^{Et2}CAAC)Au(carbazolide), is synthesized with excellent stability and remarkable PL properties, including PLQY approaching unity and an excited state lifetime of 10^6 s^{-1}. [4] Furthermore, the computational outcomes are instrumental in elucidating the PL characteristics, i.e., ^{3}MLCT-character phosphorescence and variations in PLQY values, observed in fast and bright phosphorescent diamidocarbene–metal(I)–carboranyl copper and gold complexes, which show up to 68% PLQY and microsecond lifetimes. [5]

References

[1] Di, D., Romanov, A.S., Yang, L., Richter, J.M., Rivett, J.P., Jones, S., Thomas, T.H., Jalebi, M.A., Friend, R.H., Linnolahti, M., Bochmann, M., Credgington, D. *Science*. 356 (6334), (**2017**), 159; https://doi.org/10.1126/science.aah4345

[2] Yersin, H., Czerwieniec, R., Shafikov, M. Z., Suleymanova, A. F. *ChemPhysChem*. 18 (24), (**2017**), 3508; https://doi.org/10.1002/cphc.201700872

[3] Hossain, J., Akhtar, R., Khan, S. *Polyhedron*. 201 (29), (**2021**), 115151; https://doi.org/10.1016/j.poly.2021.115151

[4] Phuoc, N.L., Brannan, A.C., Romanov, A.S., Linnolahti, M. *Molecules*. 28 (11), (**2023**), 4398; https://doi.org/10.3390/molecules28114398

[5] Powley, S.L., Riley, C., Cho, H., Phuoc, N.L., Linnolahti, M., Greenham, N., Romanov, A.S. *Chem. Commun*. 59 (80), (**2023**), 12035; https://doi.org/10.1039/D3CC04091G

Computational approaches for the rational design of engineered silk-like proteins

Adam L. Harmat[1,2,*], Dmitry Tolmachev[1,2], Alberto Scacchi[2,3], and Maria Sammalkorpi[1,2,3]

[1]Department of Chemistry and Materials Science, Aalto University, Espoo, Finland

[2]Academy of Finland Center of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, Espoo, Finland

[3]Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland

*adam.harmat@aalto.fi, Soft Materials Modelling group, Aalto University

Condensate formation, i.e. liquid-liquid phase separation (LLPS) of protein solutions in living cells is an established pre-assembly step associated with basic biological cell function and several pathological conditions. These include, e.g., Alzheimer's disease, amyotrophic lateral sclerosis, and Parkinson's disease [1]. LLPS is also an intermediate step in the formation of advanced biobased materials, such as amyloids, mussel feet adhesives, squid beaks or silk-like fibers. Protein structural materials exhibit exceptional mechanical properties whilst being biodegradable and lightweight. The rational design of protein condensates is necessary for understanding LLPS and paving the way for engineered biosynthetic protein materials.

To this purpose, we investigate engineered silk-like proteins using computational modelling to explore molecular level interactions and their implications on LLPS as observed in experiments [2,3]. Silk-like proteins have two folded domains connected by an intrinsically disordered region (IDR), making them an ideal model system for systematically investigating the interplay of folded and disordered regions in protein assembly.

Here, we present a methodology advancement based on using protein-protein docking combined with molecular dynamics simulations to study interactions between the folded domains. We demonstrate the approach for a well-characterized ubiquitin system after which we map the response of four different folded domains matching our experimentally realized systems [4,5]. The simulations results show a difference in the type and anisotropicity of the interactions that regulate coacervate propensity and the physical properties of the coacervates. A mesoscale coarse-grained model was constructed to better understand the protein assembly process. The results highlight a complex interplay of folded and IDR domain interactions.

References

[1] Albertti, S. *Curr. Biol.* 27 (20), (**2017**), R1091-R1102.
[2] Batys, P, Fedorov, D., Mohammadi, P., Lemetti, L., Linder, M.B., Sammalkorpi M., *Biomacromolecules* 22 (2), **(2021)**, 690-700.
[3] Lemetti, L., Scacchi, A., Yin, Y., Shen, M., Linder, M.B., Sammalkorpi, M., and Aranko, A.S., *Biomacromolecules* 23 (8), **(2022)**, 3142–3153.
[4] Fedorov, D., Escalona, N.R., Tolmachev, D., Harmat, A.L., Scacchi, A., Sammalkorpi, M., Aranko, A.S., and Linder, M.B., *submitted* **(2023)**.
[5] Harmat, A.L., Tolmachev, D., and Sammalkorpi, M., *under preparation* (**2023**).

PO17

Chemistry Days Young Researcher Symposium (KP2024-YRS): The Effect of a Humidity Gradient on Tensioned Micro-Veneers

Mikko Valkonen[1], Muhammad Awais[1], and Lauri Rautkari[1]

[1]Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems;
Vuorimiehentie 1, 02150 Espoo / P.O. Box 16300, FI-00076 AALTO; Finland

Wood absorbs moisture when it interacts with water in either liquid or vapour form. Moisture absorption is a phenomenon that causes wood to swell and decreases the mechanical properties of this biomaterial [1]. In practice, moisture always propagates into wood constructs; it is impossible to mitigate this issue efficiently without, for example, chemically treating the wood [2]. The wood moisture content should be considered when replacing fossil-based products such as steel and concrete with sustainable materials like wood. Constructs like high-rise wooden buildings require a better understanding of the moisture sorption behaviour of wood under loading conditions because high-rise wooden buildings involve high-stress states.

The moisture sorption behaviour of stressed wood can be studied with long-wave thermal imaging (thermography). Herein, the heat of sorption of timber as it is subject to high relative humidity (RH), such as a 95 % RH under different loading conditions, is analysable. Methodologically, a FLIR E60 (Teledyne FLIR, Wilsonville, OR, USA) thermal camera was used to image Scots pine (*Pinus sylvestris* L.) sapwood micro-veneers of ca. 15 × 48 mm^2 ($w \times l$) and ca. 145.89 ± 2.31 µm ($n = 3$) thickness under a micro-tensile load along the grain. The load (ca. 20 to 30 N) was generated by a Deben Microtest device (Deben UK Ltd., London, UK) by setting the displacement to a constant value of ca. 0.085 mm. Simultaneously, the RH gradient (ca. 2 to nominal 95 %) was created using an initially sealed and later (after ca. 1 h) opened purpose-built drying box with ca. 5.00 l/min N_2 flushing and a RUMED® Climate Chamber 2000 (Rubarth Apparate GmbH, Laatzen, Germany). Some preliminary results of the change in temperature as a function of RH gradient subjection time are depicted in Figure 1.

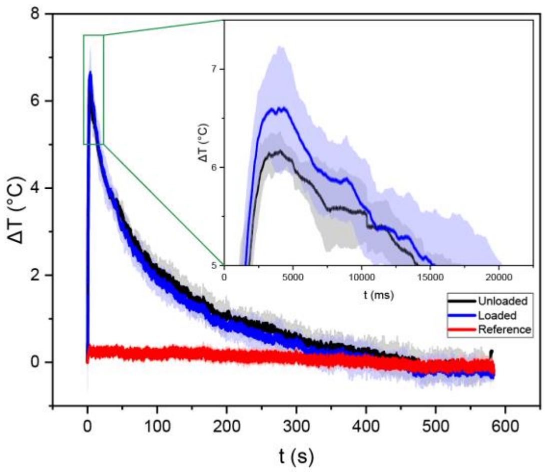


Figure 1: Temperature change as a function of subjection time to the RH gradient. The areas around the plots are the sample standard deviations for the specimens, while $N = 3$ for the specimens and $N = 6$ for the thermally inert reference.

References

[1] Wang, J. Cao, X., Liu, H. *Eur. J. Wood Prod.* 79, (**2021**), 245–59; https://doi.org/10.1007/s00107-020-01623-9.

[2] Lahtela, V. Kärki, T. *Wood Res.-Slovakia* 60 (5), (**2015**), 763–72; http://www.centrumdp.sk/wr/201505/08.pdf.

Fixed-bed column studies of heavy metal and ammonium removal by using alkali-activated adsorbent from industrial side streams

Elavarasi Sundhararasu, Hanna Runtti, Sari Tuomikoski, Teija Kangas, Ulla Lassi

University of Oulu, Research Unit of Sustainable Chemistry, P.O. Box 4300, FI-90014 Oulu, Finland

Water pollution by heavy metal contaminants is a global concern, emphasizing the urgent need for cost-effective, and eco-friendly wastewater purification solutions [1]. Using mineral industrial side streams for this purpose could promote a circular economy. With the increasing demand for efficient water treatment technologies worldwide, cost-effective alkali-activated adsorbents based on mineral industrial side streams may be employed [1,2]. This research focuses on the stability of alkali-activated materials as efficient adsorbents for nickel and ammonium removal. Industrial side streams (blast furnace slag, Linz-Donawitz slag, ladle slag, analcime) are used as raw materials. Characterization includes X-ray diffraction, X-ray fluorescence, surface area measurements, Fourier-Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy, and leaching tests.

Nickel adsorption/desorption experiments were performed in fixed bed column using 0.5 cm bed height. Flow rate (5 mL/min) and concentration (50 mg/L) were evaluated for the removal of nickel ions [1]. In the case of ammonium removal, flow rates were 5, 10 and 20 mL/min and initial concentration was 40 mg/L [2]. Alkali-activated adsorbents were regenerated in several cycles by using sodium-based regeneration agents. Experimental values were fitted with Thomas, Bohart–Adams and Yoon–Nelson breakthrough curve models and the models fitted well with the experimental data with a high R^2 value.

Batch adsorption experiments were conducted to ammonium to explore the impact of initial concentration (from 5 to 1000 g/L), adsorbent dosage (from 1 to 20 g/L) and contact time (from 1 minute to 24 hours). Ammonium adsorption onto alkali-activated analcime surfaces was analyzed through various isotherm models, including Langmuir, Freundlich, Sips, and Bi-Langmuir. Moreover, the experimental data were evaluated using pseudo-first-order, pseudo-second-order, and Elovich models [3]. The findings indicate that the alkali-activated materials are promising materials for efficiently removal of nickel and ammonium from water sources.

References

1. Sundhararasu, E.; Tuomikoski, S.; Runtti, H.; Hu, T.; Varila, T.; Kangas, T.; Lassi, U. Alkali-Activated Adsorbents from Slags: Column Adsorption and Regeneration Study for Nickel(II) Removal. *ChemEngineering* **2021**, *5*, 13, doi:10.3390/chemengineering5010013.
2. Sundhararasu, E.; Runtti, H.; Kangas, T.; Pesonen, J.; Lassi, U.; Tuomikoski, S. Column Adsorption Studies for the Removal of Ammonium Using Na-Zeolite-Based Geopolymers. *Resources* **2022**, *11*, 2–13, doi:10.3390/resources11120119.
3. Runtti, H.; Sundhararasu, E.; Pesonen, J.; Tuomikoski, S.; Hu, T.; Lassi, U.; Kangas, T. Removal of Ammonium Ions from Aqueous Solutions Using Alkali-Activated Analcime as Sorbent. *ChemEngineering* **2023**, *7*, 5, doi:10.3390/chemengineering7010005.

Blue-light induced 1,2-Chloro-*N*-Cl-amination of Olefins using *N*,*N*-Dichloro-*tert*-butylcarbamate reagents

Sini S. Irvankoski[1], Michael Davenport[2], Daniel Ess[*,2], and Juha H. Siitonen[*,1]

[1]Department of Chemistry and Material Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.
[2]Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States.

Direct amination of olefins has gathered a lot of attention in the recent years, as nearly all modern materials and pharmaceuticals contain nitrogen. Different carbamate-based aminations have found scant uses over the years but harnessing them for more widespread use in synthetic chemistry is yet to be established. In particular, *N*-chlorocarbamates have been previously applied in aminochlorinations, chlorinations, and a range of other transformations using catalytic metals (Cr, Cu), thermal activation or UV irradiation with sensitive and expensive photocatalysts.[1,2] Their broader utility in synthetic chemistry is largely limited by the lack of functional group tolerance and complications related to the required activation methods. While the homolytic cleavage of N–Cl bonds using UV light has been widely studied and even utilized in water purification, activation of N–Cl bonds using visible blue light is currently unknown.

Herein we introduce such a blue light induced aminochlorination of unactivated olefins. The method is a new functionalization tool allowing the direct installation of nitrogen atoms to olefinic molecules in a streamlined fashion. By using blue light as a mild activator, our work demonstrates that a simple reagent *N*,*N*-dichloro-*tert*-butylcarbamate can circumvent numerous of the prior issues, and a wide range of functionally diverse olefins are successfully aminochlorinated. The mechanistic studies of this transformation suggest that dichlorocarbmates undergo a photochemical excitation to yield a nitrogen and a chlorine radical which then react with the olefinic double bond. With this method aminochlorination is achieved energy effectively from readily available starting materials without harsh reaction conditions nor highly specialized chemical equipment.

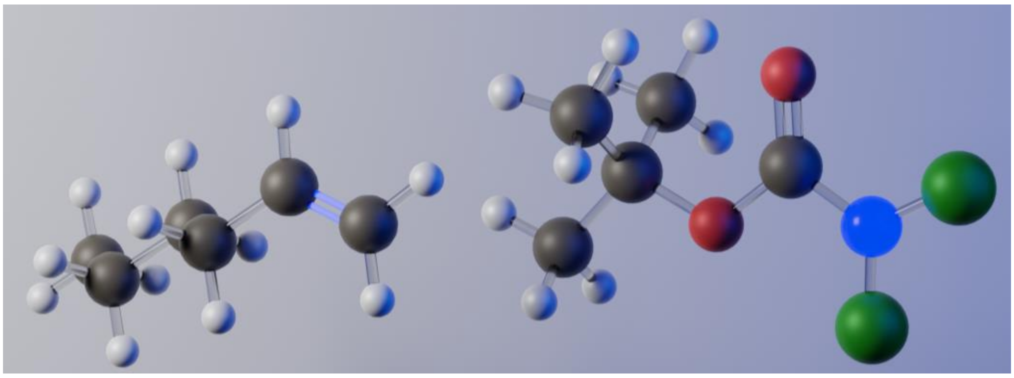


Figure 1: New blue light induced method allows direct installation of nitrogen to olefinic compounds (1-hexene, left) in a streamlined fashion using readily available starting materials (*N*,*N*-Dichloro-*tert*-butylcarbamate, right).

References

[1] Lu, X.; Xiao, B.; Zhang, Z.; Gong, T.; Su, W.; Yi, J.; Fu, Y.; Liu, L. *Nat. Commun.* 7 (1), (**2016**), 1–8; https://doi.org/10.1038/ncomms11129.

[2] Rivas, M.; Palchykov, V.; Jia, X.; Gevorgyan, V. *Nat Rev Chem*,, 6 (8), (**2022**), 544–561; https://doi.org/10.1038/s41570-022-00403-8.

Ni-rich Positive Electrode Containing Carbon Nanotubes as Conductive Additive Performance for High-power Li-ion Batteries

Sara Hamed, Tanja Kallio
Department of Chemistry and Materials Science (CMAT), School of Chemical Engineering,
Aalto University, 02150, Espoo, Finland
Sara.hamed@aalto.fi

Li-ion batteries (LIBs) nowadays have been used widely for applications such as the electric vehicles, portable electronic devices, and stationary energy storage industries because of their high energy and power density and reliable lifetime [1]. However, the current energy density and power density of LIBs less meet the performance required by portable electric devices and EVs. To meet these requirements, carbon black is a commonly used conductive agent to reduce the internal resistance of the electrode and provide electronic pathways in the electrodes through “point-to-point” contact between acetylene black and active material particles; however, it is disadvantageous because of 0D material characteristics. On the other hand, carbon nanotubes (CNTs) are promising material as a conductive agent for reducing the electrode's internal resistance due to their high aspect ratio and forming three-dimensional (3D) conductive networks by the “line-to-line” contact with other CNTs and “line-to-point” contact with active material particles [2]. Since CNT and CB are inclined to agglomerate, only CNTs or sole CBs might not be capable of efficiently building a conductive network in the electrode. It is necessary to avoid self-aggregation while constructing a three-dimensional carbon network by sufficiently utilizing the advantages of one-dimensional (1D) CNT and zero-dimensional (0D) CB.

In this study, the properties of a Li-Ni0.6Co0.2Mn0.2O2 positive electrode were investigated by varying the electrode composition. The specific capacity, coulombic efficiency, and rate capability of the electrode were significantly affected by the ratio of carbon nanotubes (CNTs) to carbon black (CB) and the total amount of the additives. The rate capability of the electrode is enhanced by increasing the amount of CNTs up to 30 wt-% in the total conductive carbon share, when the PVDF and active material amounts were fixed to 1 % and 98 %, respectively. The result is explained by the CNT additive's electronic conducting effect, which resulted in higher discharge specific capacity. The results of a long-term cycling experiment indicate that the mechanical integrity of the electrode's composition plays a crucial role in its durability. Moreover, the operando XRD and dilatometry experiments demonstrate other benefits brought by CNTs for the NMC622 positive electrodes. The presence of CNTs in the electrode reduces the irreversible height change that occurs during cycling and minimizes anisotropic lattice changes compared to the reference electrode and thus improve the capacity retention during long term cycling.

References

[1] Hou, W., Zhu, D., Ma, S., Yang, W., Yan, H., & Dai, Y. High-voltage nickel-rich layered cathodes in lithium metal batteries enabled by a sulfolane/fluorinated ether/fluoroethylene carbonate-based electrolyte design. *Journal of Power Sources, 517* (2022), 230683.

[2] Cheon, S. E., Kwon, C. W., Kim, D. B., Hong, S. J., Kim, H. T., & Kim, S. W. Effect of binary conductive agents in LiCoO2 cathode on performances of lithium ion polymer battery. *Electrochimica acta, 46*(4) (2000), 599-605

From Exfoliated Graphite to Graphene-Based Anodes for Sustainable Biophotovoltaic Applications

Sara Lund[1,2], Laura T. Wey[2], Tom Lindfors[1], Jan-Henrik Smått[1], Jouko Peltonen[1], Johan Bobacka[1], Rose-Marie Latonen[1] and Yagut Allahverdiyeva[2]

[1]Laboratory of Molecular Science and Engineering, Faculty of Science and Engineering, Åbo Akademi University, Henriksgatan 2, 20500 Turku (Åbo), Finland

[2]Photomicrobes group, Molecular Plant Biology, Department of Life Technologies, University of Turku, 20014 Turku, Finland

Due to the current climate crisis, there is an urgent demand to develop renewable energy technologies with materials that are abundant and preferably from renewable sources. In this work, graphene and graphene-nanocellulose composite films prepared by exfoliation of natural flake graphite are utilized as electrode materials in a biophotovoltaic device (BPVs) for green energy generation (Fig. 1). In a BPV device, photosynthetic microbes (e.g., cyanobacteria) convert solar energy into electricity using water as the source of electrons [1]. The electrode materials are spray-coated from few-layer graphene dispersions prepared by a green liquid-phase exfoliation method in an aqueous surfactant (sodium cholate) solution [2] or a suspension of cellulose nanocrystals (CNC) [3]. The developed shear exfoliation method is a fast and facile process which produces dispersions of high-quality few-layer graphene and graphene-CNC with a high concentration only after 2 h of exfoliation. Both CNC (extracted from cellulose) and sodium cholate are natural and non-toxic materials readily available from renewable sources. The prepared electrode films possess a high electrical conductivity and cyclic voltammetry experiments revealed that the films are electroactive and stable in aqueous electrolyte solutions. It was also found that the films are hydrophilic possessing roughness in nanoscale which are preferable qualities for anode materials in BPV devices. The average photocharge densities generated from illuminating the biofilms of cyanobacteria on the few-layer graphene and graphene-CNC films were 86.0 ± 32.0 μC cm^{-2} and 52.8 ± 23.2 μC cm^{-2}, respectively.

[1] Wey et al., ChemElectroChem, 6, 5375–5386 (2019)
[2] Lund et al., Carbon, 174, 123–131 (2021)
[3] Lund et al., Carbon Trends, 9, 100210 (2022)

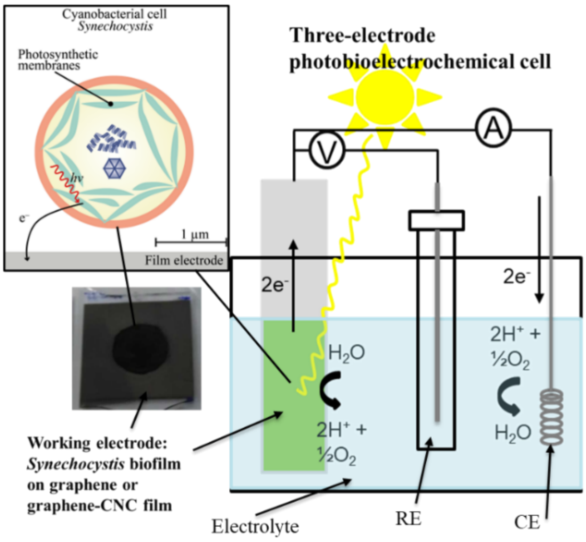


Fig. 1. Schematic representation of a cyanobacterial cell and a three-electrode biophotovoltaic system with a photograph of graphene-CNC working electrode coated with a biofilm of cyanobacterial cells